Short Communication

Kelvin-Helmholtz Instability of Langmuir Monolayers

Shigeyuki Komura ([1],*) and Takahiro Iwayama ([2])

([1]) Department of Mechanical System Engineering, Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology, Iizuka 820, Japan
([2]) Department of Control Engineering and Science, Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology, Iizuka 820, Japan

Abstract. — We discuss the possibility of Kelvin-Helmholtz instability of a Langmuir monolayer. Even for a positive surface tension, this instability is expected to occur above a critical value of the velocity of the upper air relative to the water. This is in contrast to the buckling transition which occurs for a negative surface tension.

Many amphiphilic molecules form a monomolecular layer at an air-water interface when they are only slightly soluble in the bulk water. Such an insoluble film is called a Langmuir monolayer and has attracted both academic and technological interests [1].

Although Langmuir monolayers exhibit various important class of two-dimensional phenomena [2], their fluctuation and morphology into third dimension have also attracted great interests both theoretically and experimentally. For instance, Milner *et al.* predicted a buckling of Langmuir monolayers in a fluid phase under a lateral compression which decreases the surface tension to $\gamma = \gamma_0 - \Pi$, where γ_0 is a surface tension of pure water and Π is a two-dimensional surface pressure due to the compression [3]. As the surface tension γ becomes very low and even negative, the system intends to increase its interfacial area and the interface turns out to be unstable. The physical process in this instability is similar to that of a plate under compression.

In a real system, however, buckling was never observed in fluid monolayers and they collapse to form multilayers even at positive tensions ($\gamma_0 > \Pi$) upon increasing the surface pressure. Experimentally, the buckling transition has been found in other types of monolayers such as by Bourdieu *et al.* [4] in polymerized monolayers using X-ray scattering, or by Saint-Jalmes *et al.* in solid monolayers using light scattering [5]. Formation of multilayers may be suppressed for these types of monolayers and the buckling takes place at positive γ. Recently, Hu and Granek have predicted the buckling modulation of monolayers due to the head-tail asymmetry [6].

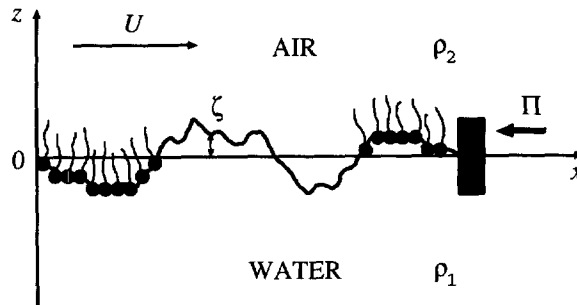(*) Author for correspondence (e-mail:komura@iizuka.isc.kyutech.ac.jp)

Fig. 1. — Schematic representation of a Langmuir trough. Π is the surface pressure and U is the velocity of the air (with density ρ_2) relative to the water (with density ρ_1) in the x-direction. $\zeta(x)$ denotes the displacement of the interface in the z-direction.

They anticipated an hexagonal array of long-finger structure induced by non-zero spontaneous curvature of the monolayer.

So far, the problem of monolayer instability has been limited within static arguments. In this article, we discuss the possibility of a dynamical instability of Langmuir monolayers, which has completely different physical origin compared to the static instabilities mentioned above. This instability is generally known as "Kelvin-Helmholtz instability" which occurs when two superposed fluids flow one over the other with a relative horizontal velocity [7,8]. The physical mechanism of this instability has been described by Batchelor in terms of vorticity dynamics [9]; the accumulation process of vorticity at certain points on the interface and of rotation of neighbouring points occur together, leading to exponential growth of the disturbance. For Langmuir monolayers, above a certain critical value of the velocity of the air relative to the water, the Kelvin-Helmholtz instability will arise before the static buckling transition takes place. Our result shows that the critical velocity and the wavelength of the most unstable mode are deeply affected by the presence of the adsorbed amphiphilic molecules.

It has been shown that the Kelvin-Helmholtz instability is also relevant to lyotropic liquid crystals in smectic phase (L_α phase) [10]. They discuss this instability in terms of "Reynolds effect" triggered by shear flow in which the fluctuation amplitude is amplified owing to the increase in lifetime. As a result, mixing and strong concentration fluctuations are expected to occur near the interface.

Consider a simplified Langmuir trough as depicted in Figure 1 where the surface pressure Π is exerted on the monolayer along the x-axis. We assume that the Langmuir monolayer is in its fluid phase. Let us denote by U the velocity of the air in the x-direction relative to the water and by $\zeta(x)$ the displacement of the interface in the z-direction. We assume a uniform displacement along the y-direction, and the depth of the water is taken as infinite. We describe here both the air and the water as incompressible inviscid fluids. Since the flow is uniform, both of the velocity fields are rotation free, and can be conveniently expressed in terms of the velocity potential as $\mathbf{v}_i = \mathbf{grad}\ \phi_i$, with $\nabla^2\phi_i = 0$ ($i = 1, 2$). Hereafter the lower indices 1 refer to the water and 2 to the air, respectively. We assume that the wind does not cause any flow of amphiphilic molecules on the surface. In fact, this flow can induce a backflow in the bulk water [2]. As in reference [11], we seek the velocity potential in the form

$$\phi_1 = A_1 e^{kz} \cos(kx - \omega t), \tag{1}$$

$$\phi_2 = A_2 e^{-kz} \cos(kx - \omega t) + Ux. \tag{2}$$

The z-component of the velocity of the water and the air at $z = 0$ are

$$v_{1z} = \frac{\partial \phi_1}{\partial z} = \frac{\partial \zeta}{\partial t}, \tag{3}$$

$$v_{2z} = \frac{\partial \phi_2}{\partial z} = U\frac{\partial \zeta}{\partial x} + \frac{\partial \zeta}{\partial t}. \tag{4}$$

Next we consider the force balance condition at the interface including the force due to the monolayer. For this purpose, we use the deformation energy of the monolayer given by the well-known Helfrich Hamiltonian [12]:

$$F = \gamma \int dA + \frac{\kappa}{2} \int (c_1 + c_2 - c_0)^2 dA. \tag{5}$$

In the above, dA is the surface element, κ is the bending rigidity, c_1 and c_2 are two principle curvatures, and c_0 is the spontaneous curvature. By using this equation, Ou-Yang and Helfrich have obtained the generalized Laplace's formula given by [13]

$$P_1 - P_2 = -2\gamma H + \kappa(2H + c_0)(2H^2 - 2K - c_0 H) + 2\kappa \nabla^2_{\mathrm{LB}} H, \tag{6}$$

where P_i are the pressures, $H = -(c_1 + c_2)/2$ is the mean curvature, K is the Gaussian curvature, and ∇^2_{LB} is the Laplace-Beltrami operator on the surface. The expressions for P_i are provided by the Bernoulli's equations which satisfy the boundary condition at $z = 0$ when $\zeta = 0$ [11]. After the linearization with respect to ζ in equation (6), the condition of the force balance at $z = 0$ becomes [14]

$$\rho_1 \frac{\partial \phi_1}{\partial t} + \rho_1 g\zeta - \left(\gamma + \frac{\kappa c_0^2}{2}\right)\frac{\partial^2 \zeta}{\partial x^2} + \kappa \frac{\partial^4 \zeta}{\partial x^4} = \rho_2 \frac{\partial \phi_2}{\partial t} + \rho_2 g\zeta + \frac{\rho_2}{2}(v_2^2 - U^2), \tag{7}$$

where ρ_i are the respective densities and g is the acceleration of gravity. One can also take into account the fluctuation of the surface tension owing to the fluctuation of the surface density of amphiphilic molecules, namely, the compressibility of the monolayer [14]. This, however, only gives rise to higher order contribution to equation (7) as long as the reference state of the interface is planer. Moreover, κ can also depend on the total area of the interface and hence on Π [3], but this effect will be neglected for simplicity. One finds from equation (7) that the spontaneous curvature merely shifts (upward) the surface tension within the lowest order calculation.

Following the same procedure as in reference [11], we look for the displacement ζ in the periodic form $\zeta = a\sin(kx - \omega t)$. Notice that only terms of the first order in A_2 are retained in evaluating $v_2^2 - U^2$ in equation (7). After some calculation, we obtain the dispersion relation given by

$$\omega = \frac{k\rho_2 U}{\rho_1 + \rho_2} \pm \sqrt{\frac{kf(k)}{\rho_1 + \rho_2}}, \tag{8}$$

with

$$f(k) = \kappa k^4 + \left(\gamma + \frac{\kappa c_0^2}{2}\right)k^2 - \bar\rho U^2 k + \Delta\rho g, \tag{9}$$

where $\bar\rho = \rho_1\rho_2/(\rho_1+\rho_2)$ and $\Delta\rho = \rho_1 - \rho_2$. If ω is a complex number with a positive imaginary part, the motion becomes unstable and this is called Kelvin-Helmholtz instability. Hereafter we shall only discuss the case of vanishing spontaneous curvature ($c_0 = 0$) just for the simplicity.

Results for several special cases can be deduced from equation (8). First, we consider the static case where the air is at rest, *i.e.* $U = 0$. If the surface tension satisfies $\gamma < \gamma_c = \gamma_0 - \Pi_c = -2(\kappa \Delta \rho g)^{1/2}$, $f(k)$ can be negative for a certain range of the wave vector k. The most unstable mode is given by $k_c = (\Delta \rho g/\kappa)^{1/4}$ in this case. This situation exactly corresponds to the buckling instability predicted by Milner *et al.* [3] and occurs only for mechanical reason due to the lateral compression of the Langmuir monolayer. This is not a dynamical instability. Notice that the expected critical surface tension is negative although it is extremely small, and the buckling instability is expected to occur at the vanishing surface tension in practice [3].

When there are no amphiphilic molecules, as originally considered by Kelvin, the interfacial property is solely determined by the surface tension of water, γ_0. In this case, $f(k)$ can be negative provided $U > U_{c1} = (4\gamma_0 \Delta \rho g/\tilde{\rho}^2)^{1/4}$, and the most unstable mode is $k_{c1} = (\Delta \rho g/\gamma_0)^{1/2}$ [7-9, 11]. Typical values for air over water ($\rho_1 \sim 1$ g cm^{-3}, $\rho_2 \sim 10^{-3}$ g cm^{-3}, $\gamma_0 \sim 74$ dyn cm^{-1}) provide $U_{c1} \sim 730$ cm s^{-1} and $k_{c1} \sim 3.6$ cm^{-1} ($2\pi/k_{c1} \sim 1.7$ cm). (Roughly these values were originally predicted by Kelvin.) Although the compressibility and the viscosity of the air has been neglected in the calculation, the above critical velocity gives a good estimate for the onset of the instability [7].

As the surface pressure Π is increased towards γ_0 in the presence of adsorbed amphiphilic molecules, it turns that the interface is mainly governed by the bending rigidity κ. In principle, for any value of γ, there exists a certain critical U_c above which the interface becomes unstable. Here we consider the case for $\gamma = 0$ which is still larger than γ_c at which the static buckling takes place. In this case, the critical velocity is

$$U_{c2} = (2/3^{3/8})\kappa^{1/8}\tilde{\rho}^{-1/2}(\Delta \rho g)^{3/8}, \qquad (10)$$

and the most unstable mode is $k_{c2} = (\Delta \rho g/3\kappa)^{1/4} = k_c/3^{1/4}$. With the same orders of magnitude as used before, and $\kappa \sim 10^{-13}$ erg, we find that $U_{c2} \sim 13$ cm s^{-1} and $k_{c2} \sim 7.6 \times 10^3$ cm^{-1} ($2\pi/k_{c2} \sim 8 \times 10^4$ Å). This length scale is accessible with current experimental techniques [4,5]. Comparing with the pure water surface case, we see $U_{c1} \gg U_{c2}$ and $k_{c1} \ll k_{c2}$ indicating a dramatic effect of adsorbed amphiphilic molecules on the surface property. One can expect a crossover of these critical values by changing the surface pressure Π.

The zero surface tension case is also realized in the saturated oil-water interfaces in microemulsions [15]. Assuming a flat oil-water interface, it can be destabilized with smaller U_{c2}, since the density difference ($\Delta \rho$) is smaller for the oil-water interface than the air-water interface. This type of instability may be also relevant to monolayers at oil-water interfaces in bicontinuous microemulsions under shearing deformation [16].

In summary, we have discussed the possibility of Kelvin-Helmholtz instability of a Langmuir monolayer. This instability is expected to take place above a critical velocity of the air relative to the water. The critical velocity is deeply affected by the presence of amphiphilic molecules and also by the exerted surface pressure.

References

[1] For reviews, see for instance, Knobler C.M., *Adv. Chem. Phys.* **77** (1990) 397; Möhwald H., *Ann. Rev. Phys. Chem.* **41** (1990) 441; McConnell H.M., *Ann. Rev. Phys. Chem.* **42** (1991) 171; Knobler C.M. and Deshai R., *Ann. Rev. Phys. Chem.* **43** (1992) 207.

[2] Andelman D., Brochard F., Knobler C.M. and Rondelez F., in "Micelles, Membranes, Microemulsions, and Monolayers", W.M. Gelbart, A. Ben-Shaul and D. Roux, Eds. (Springer-Verlag, New York, 1994) p. 559.

[3] Milner S.T., Joanny J.-F. and Pincus P., *Europhys. Lett.* **9** (1989) 495.

[4] Bourdieu L., Daillant J., Chatenay D., Braslau A. and Colson D., *Phys. Rev. Lett.* **72** (1994) 1502.

[5] Saint-Jalmes A., Garner F., Gallet F. and Houchmandzadeh B., *Europhys. Lett.* **28** (1994) 565.

[6] Hu J.-G. and Granek R., *J. Phys. II France* **6** (1996) 999.

[7] Chandrasekhar S., Hydrodynamic and Hydromagnetic Stability (Dover Publications, New York, 1961).

[8] Drazin P.G. and Reid W.H., Hydrodynamic Stability (Cambridge University Press, New York, 1981).

[9] Batchelor G.K., An Introduction to Fluid Dynamics (Cambridge University Press, New York, 1967).

[10] Bruinsma R. and Rabin Y., *Phys. Rev. A* **45** (1992) 994.

[11] Landau L.D. and Lifshitz E.M., Fluid Mechanics (Pergamon Press, New York, 1987).

[12] Helfrich W., *Z. Naturforsch. C* **28** (1973) 693.

[13] Ou-Yang, Zhong-Can and Helfrich W., *Phys. Rev. A* **39** (1989) 5280.

[14] Seki K. and Komura S., *Physica A* **219** (1995) 253; Komura S., in "Vesicles", M. Rosoff, Ed. (Marcel Dekker, New York, 1996) p. 197.

[15] de Gennes P.G. and Taupin C.J., *J. Phys. Chem.* **86** (1982) 2294.

[16] Kodama H. and Komura S., *J. Phys. II France* **7** (1997) 7.