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Liquid Transportation on a Material Surface Having a Spatial Gradient in Its Surface Energy

by

Tatsuki ARITA*1, Shouta YAMANAKA*1 and Itaru JIMBO*2

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Abstract

A series of experiments was carried out on the transportation of a liquid droplet on a substrate having a spatial gradient in its surface free energy. The substrate was prepared by a silanization process. The basic concept of the calculation for droplet transportation is discussed. The capability of a surface to cause motion of a droplet is examined using several key parameters such as contact angle and surface free energy gradient. The gradient surface was observed using an atomic force microscope to determine the silane coverage. Measurements showed that it is possible to predict the variation of the total surface energy of the system and that the rate of decrease of energy can be calculated for the gradient surface.

Keywords: liquid transportation, surface tension, surface energy gradient, drop movement

1. Introduction

In the previous works, the authors' group made an attempt to effectively enhance gas bubble migration from one liquid phase to another phase, where gas bubbles can be absorbed or engulfed in the second immiscible liquid droplets which have the lower surface tension than the bulk liquid phase[1]. One of the fundamental points is that the difference in surface tension between two immiscible liquid phases can play a major role in gas bubble separation and removal, which can cause the decrease in total surface energy of the system along with the spontaneous migration of the bubbles[2,3].

In case where solid, liquid and gas coexist in a system, a similar situation can be realized if there is a spatial gradient in surface tension exists on the solid surface. Based on the Young's equation, such a situation can be fully investigated. In some cases, a liquid droplet placed on the solid surface shows a spontaneous transportation because of the decrease in total surface energy of the system, as seen in the case of bubble migration between two immiscible liquids under microgravity. As realized, this kind of spontaneous transportation of liquid will be very promising for any possible applicable schemes, for it requires no power supplies or complicated mechanisms.

*1 Graduate School of Engineering, Tokai University
*2 Department of Materials Scicene, Tokai University

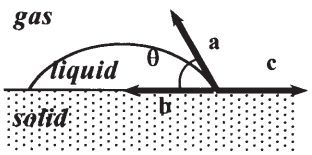

Figure 1: Young's equation at a planar surface

2. Principle

2.1 Calculation scheme

In the material processing in space, the conventional extractive metallurgy cannot be simply applied in the same way as it is accomplished on the ground where the difference in the physico-chemical properties is combined with the gravitational effect driven by the difference in density. Under microgravity, however, the interfacial tension (the interfacial energy) can play a significant role in the metallurgical processes where difference in the interfacial energy (the Helmholtz

free energy) between the separated phases may be potential measures for separation and purification during the processes.

In case where the reduction in the interfacial energy is a major driving force and the gravitational effect can be negligible, one can realize that utilization of interfacial energy reduction should also be effective for the transportation of liquid mass or gas bubbles. Based on the configuration for the Young's equation shown in Figure 1, one can calculate the total surface energy of the system F, where a, b and c stands for surface tension of the liquid, interfacial tension between the liquid and the solid, and surface tension of the solid. S_0 is the surface area of the solid. S_{gl} and S_{sl} stand for the interfacial areas between gas and liquid, and between solid and liquid, respectively.

$$F = aS_{gl} + (b-c)S_{sl} + cS_0 \quad (1)$$

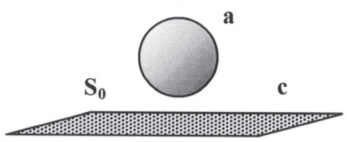

Figure 2: A droplet levitated above the surface

A simple calculation can make a comparison between the cases under microgravity for wetting and levitating. Suppose a liquid droplet wets on a solid surface with a certain contact angle θ, where the liquid surface forms a spherical surface under microgavity (Figure 1). The equivalent volume of the liquid can also be levitated above the solid surface under microgravity (Figure 2). For these configurations, one can demonstrate that any combination of the corresponding surface and interfacial energies and the contact angle leads to a result that the total surface energy for the wetting system shown in Figure 1 is smaller than that for the levitating system shown in Figure 2. The important fact is that, even if the total surface energy varies between the cases shown in Figures 1 and 2, a spontaneous transportation or movement of the liquid droplet cannot happen as long as the droplet above the solid surface does not at least get in contact with the solid. In this case, the possible reduction of the total surface energy cannot necessarily realize the droplet transportation or the movement.

2.2 The surface with a spatial gradient in surface free energy

Transportation of a liquid droplet on a substrate having a spatial gradient in its surface free energy has been pointed out in a number of works[4-6]. This kind of surface has a promising applicability by forming into various shapes to transport liquid or even bubbles under microgravity. The idea of such substrate surface has been initiated in 1984 by Swedish workers for an immunochemical purpose where a methylsilane gradient is obtained on a silicon plate[7]. The wettability of water to the surface can be characterized to continuously vary from hydrophilic to hydrophobic properties. The major concept of this fabrication is to produce surface tension of a solid substrate as its surface can form a spatial gradient, which causes droplets of water placed on it to move toward the higher surface tension area. Modification of the concept has been developed into many other surface making methods.

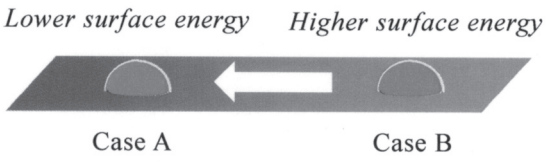

Figure 3: A droplet on the surface with a spatial gradient in surface tension

2.3 Young's equation with a gradient surface

For the case where a droplet is placed on a surface with a gradient in surface tension, as shown in the previous chapter, a similar calculation can be accomplished for the two following cases.

(1) If the difference between b and c is constant:

For the convenience in calculation, if the difference between b (the interfacial tension between the liquid and the solid) and c (the surface tension of the solid) is set to be constant, the calculation result for the case A (the droplet placed on the lower surface tension area) and the case B (the droplet placed on the higher surface tension area) in Figure 3 is that the total surface energy of the system is all the same for the two cases. This can be interpreted from the Young's equation.

$$a\cos\theta + (b-c) = 0 \quad (2)$$

If b minus c is constant, a cos θ has to be constant, which in turn means the contact angle θ does not vary as liquid surface tension a does not vary. Accordingly, the total surface energy of the system will not change from Eq. (1) even if there is a spatial gradient in the surface tension for the solid surface; i. e., there should not be any driving force for the droplet transportation as long as the difference between b and c does not vary.

(2) If the difference between b and c varies:

As realized, the above case can rarely be observed but the difference between b and c can vary along with the gradient surface. In such cases, it is clear from the Young's equation (Eq. (2)) that the difference becomes larger because the contact angle θ turns to be smaller when increasing the surface energy of the solid. Accordingly, the total surface energy of the system can

decrease along with the surface tension increase of the solid surface. This kind of decrease in the total surface energy can play a role as a possible driving force to make transportation of the droplet on that surface.

3. Experiment

The preparation of the gradient in a solid surface was accomplished by silanization of slide glass, where the vapor of decyltrichlorosilane could diffuse over a glass surface to make the surface tension gradient forming a hydrophobic- hydrophilic variation. Here, the slide glass is the one usually used for the optical microscope observation. A simple closed space was prepared with a plastic case and the temperature of the atmosphere was controlled at 30 or 40℃ with relative humidity less than 20%. The same scheme was applied to establish the gradient in a glass tubing. This silanization scheme presented in this paper is quite a simple way of preparation, while a rather complicated method has been described in a previous work [4]. A video camera captured the images when a 6 μ liter of water droplet was placed from a microsyringe onto the flat surface. Image capture was also made to observe the liquid transportation through a tubing 2.2 mm OD, 1.1mm ID with the same volume of water droplet. Replayed images were analyzed.

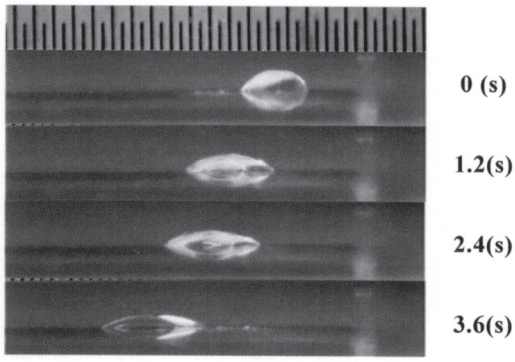

Figure 4: An example of the observation of droplet transportation on the gradient surface with a time scale.

4. Results and discussion

4.1 Calculation on the gradient surface

An example of the observation of the transportation of water droplet and the typical measurement results are shown in Figures 4 and 5, respectively. As pointed out, this kind of droplet transportation cannot necessarily happen on any solid surfaces with a gradient in the surface tension. It was observed during the contact angle measurement that the receding angles were larger than the advancing angles with the difference becoming smaller as the droplet proceeds. Because of this relationship, the cosine values for the advancing contact angles are always larger than those for the receding angles. Except for such empirical tendencies, however, has not the theoretical treatment yet revealed the reliable measures to judge the capability of the transportation for each case.

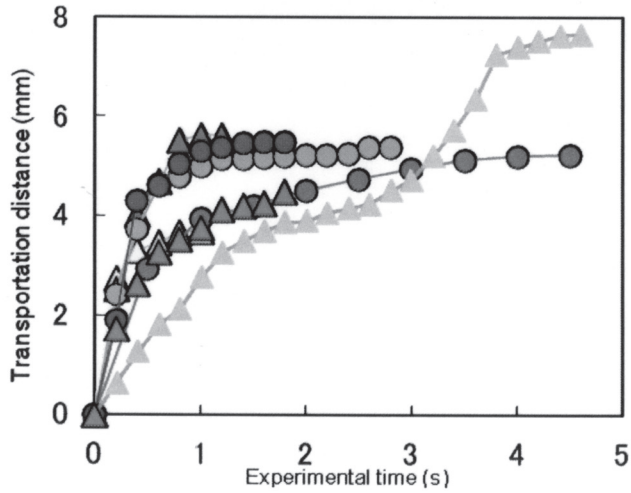

Figure 5: An example of the droplet transportation on the gradient surface (The triangles and circles stand for data of 30 and 40℃, respectively.)

The variation in the total surface energy of the system can be predicted by means of the consideration discussed in the above chapters. Assuming that the Young's equation is valid for each continuous time frame observed during the droplet transportation, at least the decrease in the total surface energy can be demonstrated. Based on Eq. (2), one can realize

$$b - c = -a\cos\theta \quad (3)$$

Even if the values of b and c vary along with the location on the surface in contact with the liquid. Here, a is a constant value and the cos θ is measurable during the observation assuming the average value within the experimental errors. Thus, the total surface energy can be calculated after inserting Eq. (3) into Eq. (1) as

$$F = a(S_{gl} - S_{sl}\cos\theta) + \int_{s0} c\,dS \quad (4)$$

where the second term in the right hand side is the total surface energy of the gradient solid itself. Even if the calculation for such a term is not possible at present, the variation (or the decrease) in the total surface energy ΔF is still measurable from the observation. Figure 6 shows the variation (or the decrease) in the total surface energy of the system obtained from the measurement. The total surface energy of the system where the gradient surface was produced by a simple diffusion process of silane seems to decrease linearly along with the distance. The spatial decrease in the total energy (i.e., the average slope of the regression lines) was found to be -5×10^{-8} J/mm, which may be the first time that the spatial gradient of the system along with the droplet movement is calculated. The authors tried in the

preliminary works to find out the effect of the droplet mass. The finding was that the observed relationship between the moving distance and the decrease in the total energy was almost the same; i. e. the calculated value of slope did not change much. This suggests that there may be the appropriate range in the spatial gradient of the surface tension, which exclusively allows the droplet transportation.

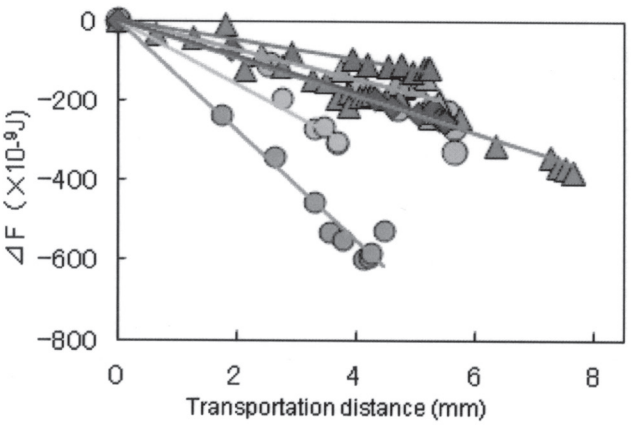

Figure 6: Variation in the total surface energy of the system as a function of distance from the point on the surface where the droplet was placed. (The triangles and circles stand for data of 30 and 40℃, respectively.)

4.2 Observation of the gradient surface with AFM

Figure 7 explains the variation of silanized spots as a function of distance. The pictures were taken through the observation using an atomic force microscope AFM. The pictures are layed out for sample surfaces at every 5 mm in distance from the silanization origin for the cases of 30 (left) and 40℃ (right). One can see the decrease in the spotted area from the top (A) to the bottom (E) as the distance increases, which in turn shows the extent of silanization.

From these pictures, the coverage of the spotted area was measured. The result is shown in Figure 8. As can be seen, the fraction of the covered area with the silan decreases linearly as a function of distance from the silanization origin, which directly corresponds to the linear decrease in the total surface energy of the gradient surface. The measured fraction was less than 1 % of the total area.

It is hard to believe that if the surface properties change to the extent of 1%, the surface can change drastically from hydrophilic to hydrophobic. Contact angle for a liquid on a composite surface can be calculated with Cassie's law[8], which implies the change in contact angle for this kind of gradient surface with a small fraction of inhomogeneous coverage will not change much. However, the difficulty may be solved in case where the apparently silanized spots could affect spatially towards the peripherical areas much larger than its coverage in a different manner.

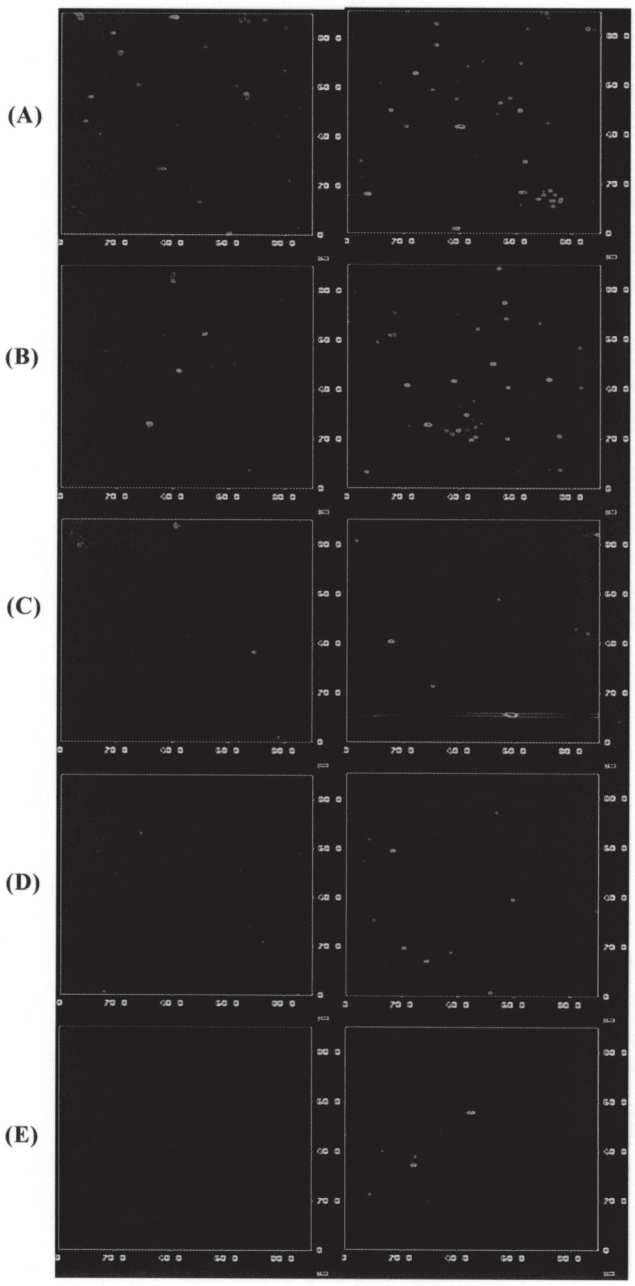

Figure 7: Observed silanized spots as a function of distance from the silanization origin; the surfaces of 30℃(left) and 40℃ (right). Pictures are taken at every 5 mm from the origin.

4.3 Transportation in a glass tubing with a gradient surface

The liquid transportation through the gradient tubing was also observed. Figure 9 shows a series of images taken at every 0.2 second during the movement. From these images, it is clear that liquid transportation was successfully accomplished even through the glass

tubing. In this case, about 4 μ liter of water moved from the left to the right by ca. 7 mm in 0.6 second. The gradient in the surface energy inside the tubing can be

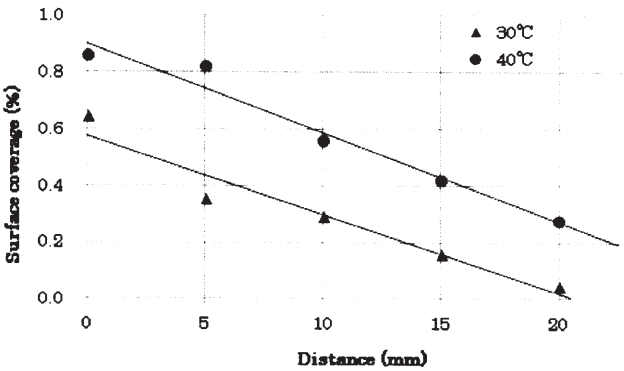

Figure 8: Observed surface coverage with silane as a function of distance from silanization origin.

calculated if the contact angle between the liquid inside and the inner wall of glass tubing. The authors tried several runs to attempt the measurement. However, an accurate measurement of the contact angle was not simple. Further experimental development should be necessary.

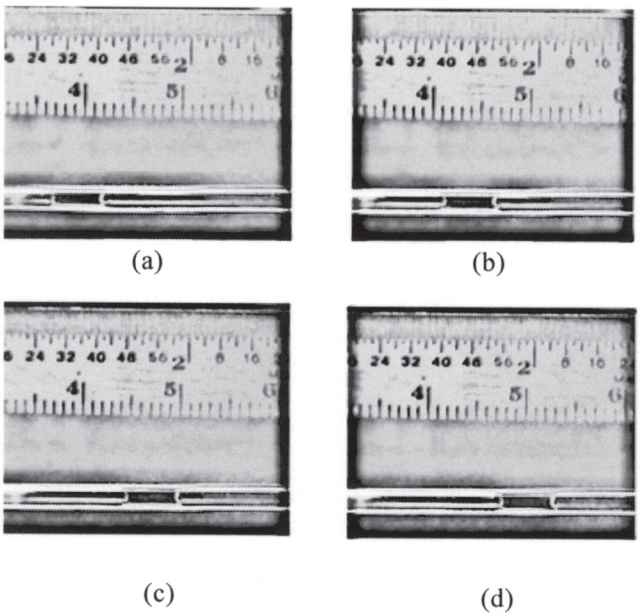

Figure 9: Liquid transportation through a glass tubing with gradient surface; water moved from the left to the right: from (a) to (d). Images were taken every 0.2 second.

5. Closing Remarks

A number of experiments were accomplished in order to develop a fundamental understanding on droplet transportation with thermocapillarity and surface tension related forces. As expected from thermodynamic consideration based on the Young's equation, the decrease in the total surface energy of the system could play a major role to transport a small amount of liquid on a gradient solid surface. It is demonstrated that the decrease in the total surface energy can be quantitatively treated assuming the validity of the Young's equation during the droplet transportation. The decreasing rate in the total energy in contact with water was found to be in the range of -5×10^{-8} J/mm for this kind of silanization gradient surface. A successful liquid transportation was also observed through the gradient tubing.

6. References

1. K. Kudo, K. Date and I. Jimbo: "Gas Bubble Removal using Suspended Droplets under Microgravity," Space Utilization Research (Proceedings of the Nineteenth Space Utilization Symposium), Vol. 19, pp. 189-192, 2003.
2. K. Kudo, K. Date and I. Jimbo: "Gas Bubble Removal using Suspended Droplets under Microgravity," Proceedings of the 16th ESA Symposium on European Rocket and Balloon Programmes and Related Research Utilization Symposium), European Space Agency, SP-530, pp. 91-93, 2003.
3. T. Origuchi, K. Kudo and I. Jimbo: "Gas Bubble Removal using Suspended Droplets under Microgravity," Proceedings of the 55th International Astronautical Congress, IAC-04-J.4.05, Canadian Aeronautics and Space Institute, 2004.
4. M. K. Chaudhury and G. M. Whitesides: "How to Make Water Run Uphill," 256, Science, 1992, pp.1539-41.
5. K. Ichimura, S-K. Oh and M. Nakagawa: "Light-Driven Motion of Liquids on a Photoresponsive Surface," 288, Science, 2000, pp.1624-26.
6. T. Yasuda, K. Suzuki and I. Shimoyama: "Droplet Transportation Induced by a Gradient in Surface Free Energy," Proceedings of the 20th Sensor Symposium, 2003, pp.249-252.
7. H. Elwing, S. Welin, A. Askendal, U. Nilsson, and I. Lundstrom: "A Wettability Gradient Method for Studies of Macromolecular Interactions at the Liquid/Solid Interface," 119, J. Colloid Interface Sci., 1987, pp. 203-210.
8. Cassie, A. B. D. and Baxter, S. "Wettability of porous surfaces," Transactions of the Faraday Society, 40, 1944, p.546.