Interfacial Phenomena and Fluid Control in Micro/Nanofluidics

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Fundamental aspects of rapidly advancing micro/nanofluidic devices are reviewed from the perspective of liquid interface chemistry and physics, including the influence of capillary pressure in microfluidic two-phase flows and phase transitions related to capillary condensation.

Keywords Liquid interface, surface tension, microfluidics, nanofluidics extraction

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1 Introduction

Miniaturized chemical systems have attracted the attention of analytical chemists and engineers from various fields because of their useful features, including their amenability toward high-throughput measurements, compactness, laborsaving attributes, high reproducibility, and small sample requirements.1,2 In most systems, specific characteristics of fluids in microchannels or nanochannels have been utilized. Many review articles have been published regarding miniaturized systems and their applications.3−18 In this review, we focus on

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state-of-the-art techniques based on liquid interfaces between two immiscible fluids, which are typically aqueous/organic phases or gas/liquid phases.

Flows of aqueous/organic phases have often been utilized for solvent extraction in microfluidic systems (solvent extraction is a most widespread separation method in chemical analysis).\textsuperscript{19,20} From the viewpoint of extraction, micrometer-sized confinement is advantageous because the specific interfacial area (surface-to-volume ratio) increases with decreasing scales, and consequently, a more rapid and efficient extraction is observed.\textsuperscript{21–26} Notably, this has been demonstrated with alkali metals,\textsuperscript{27,28} minerals,\textsuperscript{29,30} rare-earth metals,\textsuperscript{31} radioactive metals,\textsuperscript{32–34} lanthanides,\textsuperscript{35–37} steroids,\textsuperscript{38} vanillin,\textsuperscript{39} derived carbamate pesticides,\textsuperscript{40,41} and polychlorinated biphenyls,\textsuperscript{42} among others.

In addition to the specific interface area, the other remarkable properties of miniaturized setups are capillary pressure and wetting.\textsuperscript{43} While volume effects such as buoyancy dominate in laboratory-scale experiments because of the density differences between phases, surface effects such as capillary pressure and wetting often govern fluid properties in microfluidic systems.\textsuperscript{24,44–46} To effectively design micro-/nanofluidic systems for accommodating micro- and nanofluid behavior, it is crucial to understand the surface effects in such a system.

In nanofluidic systems, the capillary pressure effect can be even more pronounced.\textsuperscript{47–51} For example, when a water surface is assumed (72 mN m\textsuperscript{–1}), its capillary pressure in a confined space with capillary radii of 1 μm is comparable to one atmosphere. Under this condition, the existence of a liquid interface affects the point of phase transition termed capillary condensation.\textsuperscript{52,53}

In this review, characteristics of liquid interfaces in micro-/nanofluidic systems are described. First, two-phase flow systems are introduced from the perspective of fluid control based on liquid interface characteristics. Then, related nanofluidic systems are introduced.

## 2 Two-phase Flow in Microfluidic Systems

### 2-1 Two-phase flow

When two immiscible fluids contact each other in a microfluidic channel, various flow patterns are observed.\textsuperscript{54–56} Of these, parallel and droplet flows are most common. Parallel two-phase flows seem advantageous for the integration of continuous chemical processing, such as continuous solvent extraction. By utilizing liquid interface properties discussed in this review, characteristic operations, such as sandwiching heavier liquid flow with lighter liquid flows, are possible.\textsuperscript{24,57} On the other hand, droplet flow can encapsulate molecules or some substrate particles within the droplets.\textsuperscript{59–65} Many well-written review articles have been published on the subject of droplet flow.\textsuperscript{66–68} In this review, parallel two-phase flow\textsuperscript{69–85} is considered with respect to the roles of liquid interfaces for the sake of simplified physical descriptions.

### 2-2 Capillary pressure

Let us consider a gas/liquid interface in a capillary where the inner diameter of the capillary and the contact angle of the liquid are \(d\) and \(\theta_0\), respectively (Fig. 1a). Capillary pressure \(\Delta P_c\) (Laplace pressure) pulling the interface to the left side is proportional to surface tension \(\gamma\) and inversely proportional to the radius of curvature \(r'\) by the following equation:\textsuperscript{43}

\[
\Delta P_c = \frac{2\gamma}{r'} = \frac{4\gamma \cos \theta_0}{d}.
\]

When we assume the surface tension of water to be 72.0 mN m\textsuperscript{–1} and a contact angle of 0°, \(\Delta P_c\) is 28.8 kPa for a channel diameter of 10 μm. The pressure loss\textsuperscript{46}

\[
\Delta P_L = \frac{4\gamma \Delta L}{d^2},
\]

in a cylindrical channel with diameter \(d\) of 10 μm and length \(L\) of 100 mm is 32 kPa with velocity \(v\) of 1.0 mm/s and viscosity \(\mu\) of 1 mPa s, which is comparable with \(\Delta P_c\). This comparison suggests that the capillary pressure can be one of the most dominant factors in micro-/nanofluidic systems.

### 2-3 Contact angles

In two-phase micro-/nanofluidic systems, both a moving or static contact line—the line where all three phases (fluid 1, fluid 2, and the substrate) meet—can be a significant consideration. Static (pinned) contact lines can act as a boundary for flow, while moving contact lines can lead to changing liquid morphologies depending on time-dependent flow conditions. For moving contact lines, the dynamic advancing or receding contact angles (contact line velocity dependent contact angles) should be considered but seldom are. More often, the static advancing and receding contact angles (measured at zero velocity, after the contact line has advanced or receded) are used to predict and describe wetting behavior in channels. In an ordinary laboratory-scale experiment, when a drop of fluid 1 suspended by a tube in fluid 2 (Fig. 1b-1) contacts a substrate, the drop deforms on the substrate to make a static contact angle, \(\theta_0\) (Fig. 1b-2). When the interfacial tensions between fluid 1–fluid 2, fluid 1–substrate, and fluid 2–substrate are defined as \(\gamma_{12}, \gamma_{1s},\) and \(\gamma_{2s}\) respectively, the simplest relationship is described by the well-known Young equation:\textsuperscript{45}

\[
\gamma_{1s} = \gamma_{12} + \gamma_{2s} - 2\gamma_{12}\cos \theta_0.
\]
The contact line does not move with the introduction of fluid 1 before the angle reaches the static advancing contact angles is reached (3). Increasing the droplet volume continuously, i.e. moving contact line, results in a dynamic advancing contact angle (4). Decreasing the droplet volume decreases the contact angle until the static receding contact angle is reached (3'). Decreasing the droplet volume continuously, i.e. moving contact line, results in a dynamic receding contact angle (4').

\[ \gamma_{f_2-s} = \gamma_{f_1-s} + \gamma_{f_1-f_2} \cos \theta_0. \]  

The contact line does not move with the introduction of fluid 1 before the angle reaches the static advancing angle, \( \theta_a \) (Fig. 1b-3). After the angle exceeds \( \theta_a \), the contact line proceeds with a dynamic advancing contact angle \( \theta_a' \) which is greater than \( \theta_a \) (Fig. 1b-4). Similarly, the contact line does not move while withdrawing the liquid before the angle reaches the static receding contact angle \( \theta_r \) (Fig. 1b-3'). After the contact angle decreases below \( \theta_r \), the contact line retreats with a dynamic receding contact angle \( \theta_r' \) which is less than \( \theta_r \) (Fig. 1b-4'). The difference between advancing and receding contact angles is called contact-angle hysteresis, and, because contact angle hysteresis is inherent in wetting, the equilibrium contact angle (which lies between the static advancing and receding contact angle) cannot be directly measured. Furthermore, measured contact angles are very sensitive to interfacial adsorption and so-called “aging” of microfluidic channels may be observed over time. Contact angle aging may be favorable or unfavorable for the long-term operation of microsystems and may need to be carefully considered.

When the deformation is controlled so as not to exceed the static advancing angle or be less than the static receding angle, the contact line is pinned and prevents contact line movement during deviations in hydrodynamic pressure. By utilizing this principle, various two-phase control techniques have been demonstrated as discussed in the following sections.

### 2-4 Two-phase flow in microfluidic channels

When two phases are joined in a microchannel under appropriate conditions, a parallel two-phase flow is generated in a microfluidic channel\(^ {1,24,87} \). Figure 2a illustrates a laminar two-phase flow between fluids I and II, where \( \langle v_I \rangle \) and \( \langle v_{II} \rangle \) correspond to average velocities of the fluids I and II, respectively. By assuming 2-dimensional flow and by considering the continuity of velocity and shearing stress, the relationship between the flow rate and the width of each phase can be discussed.\(^ {88} \) In order to set the ratio of the width of fluid II to that of fluid I as \( \frac{b}{a} \), the ratio of the flow rates \( R_{II-I} \) should be set as

\[ R_{II-I} = \frac{b \langle v_{II} \rangle}{a \langle v_I \rangle} = \frac{b^2}{a^2} \frac{\mu_I - 2a + 2b}{\mu_{II} b(4a + 2b) \mu_{II} + a^2 \mu_I} \]  

where \( \mu_I \) and \( \mu_{II} \) are viscosities of the fluids I and II, respectively. In microfluidic two-phase-flow applications, the interface position is often designed to be kept at the center of a microchannel (\( b = a \)). For centering the interface position, the flow rate ratio should be

\[ R_{II-I} = \frac{\mu_I + 7\mu_{II}}{7\mu_I + \mu_{II}}. \]  

When two phases join at the junction of two microchannels,
the width ratio becomes $b/a$ theoretically. When a two-phase flow with low interfacial tension such as aqueous two-phase flow is formed in a microchannel having no contact angle hysteresis, the interface position is almost controllable by changing the flow ratio. The interface position (3-phase contact line in the microchannel) fluctuates easily. Under a condition with a significant contact angle hysteresis and with high interfacial tension, the interface position is more likely to be pinned at a certain point. For simplicity, the liquid-liquid-solid contact line is assumed to be at the center of the channel. In Fig. 2b, fluid 1 is assumed to have a superior wettability on the channel wall and a lower viscosity. The graph in Fig. 2c illustrates the pressures of the two phases, depending on the position. Because the exit port is open to ambient pressure ($P_0$), the pressures of the two phases are equal to it. To the contrary, the pressure of fluid 2 in the channel is higher than that of fluid 1, because the pressure loss per unit length (slope of the pressure loss in Fig. 2b) increases with viscosity. Thus, the pressure difference between the two phases is higher upstream ($\Delta P_a$ at $z = z_a$) and lower downstream ($\Delta P_b$ at $z = z_b$). The interface at each point bends to generate the corresponding Laplace pressure, which compensates for the pressure difference. As discussed in Sect. 2.3, the interface can bend to retain the contact angle at values between $\theta_a$ and $\theta_r$.

An example of a parallel two-phase flow in a 250-μm-wide channel is shown in Fig. 3a. In this case, there is a fast and efficient reaction that utilizes the high specific interface area between the aqueous and organic phases. Here, the aqueous solution of 4-nitrobenzene diazonium tetrafluoroborate and methylacetate containing 5-methylresorcinol are joined at the junction of a Y-shaped microchannel. The 5-methylresorcinol is partitioned to the aqueous phase and reacts with the diazonium moiety to produce an azobenzene-containing compound (Fig. 3b). The product of this reaction is electrically neutral and is extracted into the nonpolar organic phase. The specific interfacial area in the microsystem is large, and the extraction proceeds very rapidly. A nearly quantitative yield of the product was obtained in the microfluidic system, while an insoluble precipitate was generated in bulk experiments because of slow extraction and the second addition of the diazonium compound in the aqueous phase.

As a whole, such systems are widespread in microchip-based chemical analysis with various detection techniques like laser-induced fluorescence, optical photometry, and thermal lensing, and also for the implementation of chemical synthesis. Apart from water-organic systems, parallel two-phase flows are implemented in microchips for two-phase aqueous systems based on water-soluble polymers like...
polyethylene glycols (PEGs). For instance, this promising technique is used for the high-throughput screening of enzymes and proteins in PEG-salt-protein media.

2.5 Pinning of contact line by structure and surface modifications

By utilizing an isotropic wet-etching technique, a ridge (guide) structure can be fabricated on the bottom of the channel as shown in Figs. 4a and 4b. When the liquid interface is adjusted to contact at the top of the guide, the liquid interface is pinned because the guide has a small curvature radius and can allow a wider contact angle than the flat surface. Thus, a parallel two-phase flow can be maintained in a longer channel, and complicated chemical processes can be integrated. An example of the integration of complicated chemical processes utilizing the guide structure is shown in Fig. 4c. As discussed in previous sections, a parallel two-phase flow can be maintained as long as the contact angle lies between \( \theta_a \) and \( \theta_r \), but the control ranges of the flow rates and their ratios are not so wide. Take, for example, a water/air interface in a 10-μm diameter Teflon (\( \theta_a = 120^\circ \) and \( \theta_r = 100^\circ \)) microchannel. The Laplace pressure window, LPW, is defined by:

\[
LPW = \frac{4\gamma}{d} (\cos \theta_a - \cos \theta_r)
\]

which is 9.5 kPa. For a water/air interface in a silica (\( \theta_a = 20^\circ \) and \( \theta_r = 0^\circ \)) microchannel of the same dimensions, LPW = 1.8 kPa. For parallel streams, the curvature along the direction of the channels is infinitely large and, in practice, the LPW would be half of that predicted by Eq. (6). To widen the control range of a two-phase flow, a partial surface modification to more strongly pin the liquid-liquid-solid contact line at the boundary, as shown in Fig. 5, was investigated. When half of the microchannel wall is hydrophobically modified while the other half remains hydrophilic, fluid 1 (aqueous) and fluid 2 (organic or gas) tend to flow along the hydrophilic and hydrophobic portions of the wall, respectively. Furthermore, the liquid interface is pinned at the boundary between the hydrophilic/hydrophobic areas, and the control conditions

![Diagram](image)

**Fig. 5** Schematic illustration of partial surface modification. The red section of the microchannel surface is modified with a hydrophobic group while the black one is hydrophilic.

![Diagram](image)

**Fig. 6** (a) Apparatus for a two-phase countercurrent flow. (b) Pressure change of each phase along the channel. (c) Comparison of extraction efficiencies for concurrent and countercurrent flows. (d) Dependence of theoretical plate height, \( N \), on the flow rate. Copyright (2007) Wiley. Used with permission from Ref. 103.
drastically change. For fluid 1 (aqueous) to encroach the hydrophobic side, the aqueous phase should advance over the hydrophobic surface, replacing the wetting organic phase. By contrast, for fluid 2 (organic) to encroach the hydrophilic side, the organic phase should advance over the hydrophilic surface, replacing the wetting aqueous phase. The advancing contact angles corresponding to these phenomena are very large, sometimes up to 170°.102 Thus, the $|\cos \theta_2 - \cos \theta_1|$ term in Eq. (6) becomes much larger and greatly increases the Laplace pressure window (44 kPa for water/air in a 10-μm diameter adjacent Teflon and silica channels, compared with < 10 kPa in homogenous Teflon or silica channels).

By utilizing partial surface modifications, even a countercurrent flow of aqueous and organic phases can be achieved (Fig. 6a).102,103 The principle of a countercurrent flow is very similar to that of an ordinary parallel flow (co-current) shown in Fig. 2a. When fluid 2 is introduced in the direction opposite to that of fluid 1, the pressure of fluid 2 is greater at higher $z$ positions while the pressure of fluid 1 is greater in lower $z$ positions. As long as the pressure difference can be compensated with the Laplace pressure, the countercurrent flow is viable.

While extractions that use a two-phase co-current or a droplet flow can reach a theoretical plate number of 1 only, a higher plate number $N$ is expected in an extraction with a countercurrent flow. As the flow rate of the countercurrent flow decreases (contact time increases), the plate number increases to 4.6 (Fig. 6d). Thus, this technique can be used for tuning the efficiency and rapidity of the separation in a microchannel.

3 Liquid Interfaces on Nanometer Scale

3-1 Nanofluidic systems

Nanofluidic systems have received much attention because of their extremely small volume, surface chemical and/or charge effects, and anomalous phenomena which have not been observed in lab-scale and microscale experiments. Feasibility of the nanofluidic systems has been explored intensively. Recently, nanofluidic channels have been utilized in bioseparations and preconcentrations by exploiting ion-concentration polarization in nanofluidic channels and/or at the interface between microfluidic and nanofluidic channels.104-112 For example, Han et al. demonstrated direct seawater desalination based on ion-concentration polarization,113 and Manalis et al. demonstrated protein preconcentration and a sensing device.114 Furthermore, nanofluidic channels and structures have been utilized for chromatographic and electrophoretic separations.115,116 For example, Kitamori et al. demonstrated nanofluidic sample injection and chromatographic separation in a fabricated glass microchip.117 Many well-written review articles have been published on the aforementioned solid-surface effects. Here, fluid operations and the effects of free liquid surfaces in nanofluidic channels have been reviewed, as they have received limited attention in the literature.47,50

3-2 Liquid introduction and flow control

When we consider a submicron-sized fluidic channel, adequate and novel methods are required for the introduction of liquids and to control the subsequent flow in the channel. Two techniques have improved this ability significantly. One is a combined micro-/nanostructure, where nanofluidic channels are connected in the middle of a microfluidic channel (Fig. 7a).47,50,118,119 By utilizing this structure, liquids are easily introduced into the nanofluidic channel by capillary filling.47

The other technique is a pressure-driven method, where the pressure is controlled via the liquid pressure on the microfluidic channel section, which is connected to the nanofluidic channel (Fig. 7b).46,117,120,121 By controlling the flow rate in the microfluidic channel, or by applying air pressure to the microfluidic channel under a negligible flow, a pressure-driven nanofluidic system is realized. By combining the capillary introduction and pressure-driven flow technique, the capillarity and liquid viscosity have been simultaneously measured.119 Using a similar concept, Shui et al. reported two-phase junctions in nanofluidic channels for small-droplet formation.122 Recently, an improved version of the pressure-driven flow method, where solenoid valves are installed for pressure regulation and pressure control is realized with a 10-ms temporal resolution, was reported.123 In spite of the various attractive
features of nanofluidic systems, fundamental technologies such as pressure-driven flow regulation and switching are relatively immature. However, the technologies have been rapidly improved to meet the requirements of nanofluidic bioanalytical applications.

3-3 Capillary condensation in nanofluidic systems

When a saturated vapor contacts a small pore, condensation occurs because of capillarity. The phenomenon is described by Kelvin’s equation. If the saturated pressure on a flat surface is denoted by $p_0$, and that in a nanostructure with a capillary radius of $r$ and contact angle of $\theta_0$ is denoted by $p_r$, the following equation can be written:

$$\ln \frac{p_r}{p_0} = \frac{2V_m \gamma \cos \theta_0}{RTr},$$

(7)

where $V_m$ and $\gamma$ are molar volume and surface tension, respectively.

To demonstrate the phenomenon utilizing nanofluidic systems, a fused-silica microchip was designed (Fig. 8a). In this chip, the saturated vapor is generated in the microchannel section shown in Fig. 8b, where the shallow part is hydrophobically modified and only the vapor is driven to the nanopillar part (Fig. 8c). Subsequently, the saturated vapor is condensed in the nanopillar part (Figs. 8d – 8f). The central rectangular bright area in Fig. 8d corresponds to the nanopillar area before condensation. Since the area was observed from the normal direction with tilted illumination, the reflected diffraction by the pillars showed a purple color. In Fig. 8e, a part of the area became grey (less contrast), where the void between pillars was filled with condensed liquid, because of the reduction of refractive index contrast at the area. Then, the whole of the void between pillars filled with condensed liquid as shown in Fig. 8f.

A more sophisticated system for observing saturated vapor in the nanostructure has been proposed. A system that can independently control the saturated vapor pressure and substrate temperature is shown in Fig. 9a. By measuring the temperature difference between the saturation vapor generation and evaporation, the vapor pressure in the nanostructure can be calculated. As shown in Fig. 9b, the saturation vapor obviously depends on the capillary radius and a slight deviation from theory is observed. This deviation implies some specific fluid phenomena in nanometer-sized fluids or surfaces.

Multiphase operations, including phase separation, evaporation, and condensation, will play important roles in the ongoing unification of micro-/nanofluidic technologies and energy devices such as fuel cells, heat-pipe integration, and photocatalytic energy devices, because gas/liquid/solid multiphase operations are common in such applications. For example, Mawatari et al. proposed an interesting energy device with a photocatalytic fuel generator and a fuel cell (Fig. 10). In the device, the nanofluidic channel was used for proton exchange, and the surface modification was used for the gas/liquid-phase separation.

Fig. 8 (a) Illustration of a fused-silica microchip before and after bonding. (b) Expanded view of the evaporation zone. (c) Expanded view of the nanopillar condensation zone. (d) Micrograph before condensation. (e) Micrograph during condensation (some of the nanopillars are filled with liquid). (f) Micrograph after condensation (whole nanopillars are filled with liquid). Reproduced from Ref. 52, with permission of The Chemical Society of Japan.
Conclusions and Outlooks

There are many reports detailing the microfluidic applications of two-phase flows, which essentially concern liquid interface phenomena. In contrast, there are far fewer works on the mechanisms of two-phase flow, and nanofluidic applications of liquid interfaces. This review has described the current knowledge and technologies for two-phase interfaces and flows in micro-/nanofluidic systems from the perspective of interfacial chemistry and physics.

As mentioned in Sect. 2, the hydrodynamic behavior of microfluidic parallel two-phase flows can be explained by a pressure difference between the phases and the capillary pressure due to interfacial bending. With appropriate design, countercurrent flow of aqueous and organic phases can be obtained. In addition to the ordinary solvent extraction reviewed here, a characteristic extraction process utilizing nanodroplet formation is involved. This novel aqueous-aqueous extraction process will open highly effective microfluidic operations.

Liquid interface phenomena have not been widely applied, while the electrical effect of nanofluidic channels has received much attention from researchers in various fields, including separation science, biophysics, physical chemistry, and engineering for power devices, among others. Capillary introduction and capillary condensation/evaporation were reviewed in Sect. 3 as typical examples of nanofluidic phenomena related to liquid interfaces. Of course, these phenomena are not unrelated to the aforementioned fields. For example, in fuel cells, liquid water management produced during power generation can intrude gas-filled nanofluidic channels and can be removed by evaporation from the nanofluidic channel. Intensive investigations of nanofluidic systems, including their fundamental studies, are required for analytical chemistry and other applications.

Extensive studies are also required to understand micro-/nanofluidic phenomena and to establish effective design methods for future micro-/nanofluidic engineering. Specifically, in situ interfacial measurements remain a challenging issue. When surface-active species is adsorbed on the interface in the flow, interfacial tension may depend on time (position) and the model might be more complex. Measurement tools for liquid interfaces will play important roles in the superior design of two-phase flow systems. The in situ interfacial tension measurement remains a significant challenge, although some attractive image-based methods, a light scattering method, and an electrochemical method have been reported. These new challenges are expected to advance the science and technology in this field in the next years.

4 Conclusions and Outlooks

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6 References


