

There is plenty of room at the bottom: New Insights into old observations

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Abstract

Three case studies are analysed to demonstrate (1) the usefulness of fundamental understanding and theoretical modelling in systems with small dimensions, for which interfacial phenomena are crucial; (2) The possibility of advancing our understanding even in areas that are considered old; and (3) The advantages of simple theories. Copyright © 2018 VBRI Press.

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Introduction

Two trends seem to be noticeable in science in recent decades. One is focusing on small (micro- and nano-) systems, in which surface phenomena play a very important role. The other is an unfortunate decrease in the tendency to do fundamental studies, probably because of increasing funding concerns. This paper attempts to demonstrate how true is the first trend, and how the second one may lead to inefficiency.

In his famous, classic 1959 talk, Richard Feynman stated “there is plenty of room at the bottom”. By the word “bottom” he meant the world of small particles, and this statement has been used as the motto of nano-science and nano-technology. Here, I would like to boldly suggest an additional interpretation to the word “bottom”, as meaning fundamentals. This interpretation complements the original one by stating that the world of small particles requires also new insights into its fundamentals. To prevent concerns that the study of fundamentals may not lead to anything useful, it may be instrumental to follow the advice of another giant, Kurt Lewin (who is considered the father of social psychology). His famous quotation tells us that “there is nothing so practical as a good theory”!

The present paper is a review of a few independent examples of our studies that have demonstrated the value of research of fundamental issues in interfacial phenomena. Another principle that has been followed is best described by the Einstein quotation: “Everything should be made as simple as possible, but not simpler.” Thus, the theoretical (as well as experimental) models should be simple and transparent, but not at the expense of losing the physical essence of the system.

Capillary systems of limited size

Let us consider the process of inkjet printing that comprises transfer of small (order of magnitude of 10 microns) drops into a substrate that may be porous, like paper. The mechanism of penetration of the ink to the paper is the main factor affecting the print quality. If penetration is excessive, the edges of the printed symbols become fuzzy. If penetration is slow or difficult, there is a good chance that some ink will contaminate the environment (other objects, our hands, etc.).

Basically, the process is defined as penetration of a liquid into a porous medium. To model a porous medium, it is natural to think of it as a collection of capillaries. To make things as simple as possible, but not simpler, we may consider, to begin with, only a single capillary. So, the real system may be modeled, for example, by the process of liquid penetration into a single, cylindrical capillary. This process has been known and studied at least since the beginning of the 20th century (1,2).

So, what is then fundamentally new about this process? The main difference between the above general process and the inkjet process is related to the size of the drop. All previous models considered the supply of liquid to be as large as needed. The inkjet printing process is characterized by the drops being small, of the same order of magnitude as the capillary pore size. Thus, our model system (3,4) consists of a small drop penetrating a cylindrical capillary (see Fig. 1). The very important difference is that the pressure inside a large liquid reservoir is atmospheric, while the pressure inside a drop is higher than atmospheric. Thus, by being small, the drop adds a driving force for capillary penetration.

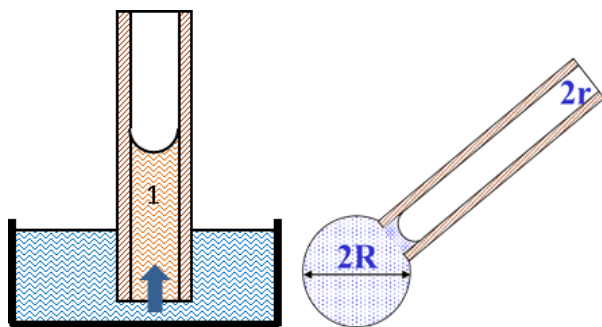


Fig. 1. Capillary penetration from limited and unlimited reservoir.

The pressure inside the drop is given by the Young-Laplace equation

$$P = P_{at} + 2\sigma/R \quad (1)$$

where P is the pressure inside the drop, P_{at} is the atmospheric pressure, σ is the surface tension and R is the radius of the drop. The pressure at the liquid side of the meniscus (point 1 in Fig. 1) is calculated from the Young-Laplace equation to be

$$P_1 = P_{at} - 2\sigma\cos\theta/r \quad (2)$$

where θ is the contact angle that the liquid makes with the solid inside the capillary, and r is the radius of the capillary. If $P > P_1$, the liquid penetrates the capillary. Thus, the penetration criterion is

$$P_{at} + \frac{2\sigma}{R} > P_1 = P_{at} - 2\sigma\cos\theta/r \quad (3)$$

or

$$\cos\theta > -r/R \quad (4)$$

Thus, when the liquid reservoir is big, ($R \rightarrow \infty$), the classical textbook criterion is achieved, namely penetration occurs only for contact angles smaller than 90° on the inside surface of the capillary. However, the novel observation in the case of a small drop is that it may penetrate the capillary even at contact angles higher than 90° .

The size of the penetrating drop determines also the kinetics of penetration. As the drop penetrates, its radius becomes smaller and smaller. This implies that the pressure in this drop becomes larger and larger. Consequently, the process is self-accelerating! Thus, the size of the penetrating drop has a major effect on the thermodynamics of capillary penetration as well as on its kinetics. This practically important knowledge resulted from studying the fundamentals.

The nano-bubble cloud

It has been known for quite some time now (e.g. 5) that stable nano-bubbles exist on a hydrophobic surface when it is dipped in water. The fact that the bubbles exist is not as surprising as the fact that they are stable for a long time.

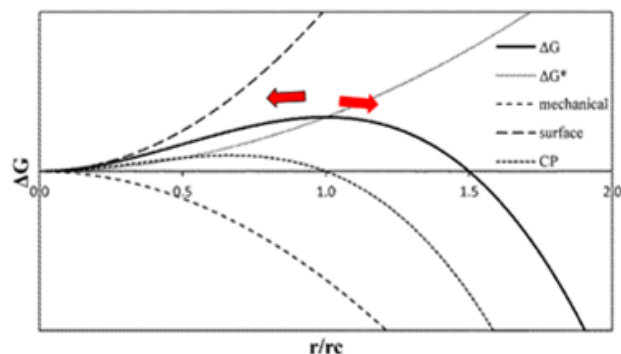


Fig. 2. Energy of formation of a nucleus of pure material.

According to the well-known equation of Lord Kelvin, when a liquid boils or vapor condenses, there exists a critical nucleus size, as shown in Fig. 2. If the radius of the actual nucleus is smaller than the critical size, the nucleus will disappear. If it is bigger than the critical size, then it will continue growing and turn into a new bulk phase. Thus, the critical point is an unstable state, as can be seen in Fig. 2, which shows that the Gibbs energy has a maximum instead of a minimum. So, what can be the source of this stability?

To explain the surprising stability of nano-bubbles, we can learn a fascinating lesson from Nature. Clouds form when water vapor condenses into water droplets. According to the Kelvin model, these droplets should either disappear or go on growing. However, an additional factor, a small amount of salt, comes into the game. This salt originates from breaking of the foam of sea waves, and is carried by winds up the atmosphere.

The crucial point is (6) that the salt is soluble in water, but completely non-volatile. Thus, salt molecules are mixed in the dispersed phase (water droplets) but do not exist in the continuous phase water vapor and air). When the volume of the drop starts to grow, the entropy of the system increases, since the salt in it has more volume to spread in. An increase in entropy decreases the Gibbs energy ($G \equiv H - TS$), where G is the Gibbs energy, H is the enthalpy, T is the absolute temperature, and S is the entropy. This decrease in G may introduce a minimum in the curve of G , as shown in Fig. 3. This explanation effect was developed by Kohler many years ago.

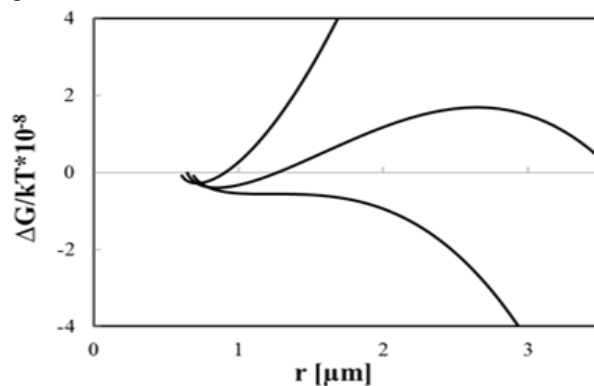


Fig. 3. Energy of formation of a vapor nucleus with various amounts of insoluble gas.

Now, what does all of this have to do with nanobubbles? The nanobubble system is approximately a “mirror image” of the droplet cloud (6). If a water-vapor bubble forms by boiling around a bubble of air, then air molecules will be mixed with water molecules in the vapor phase. In addition, we may assume that air is practically insoluble in water, therefore the amount of air in the vapor will be constant and its entropy will increase when the bubble increases. Thus, by a proper analogy and fundamental thermodynamic model, a new explanation was suggested for the stability of nanobubbles.

Super-hydrophobic surfaces

When a liquid drop spreads on an ideal solid, it reaches equilibrium at one specific contact angle (CA), called the Young contact angle. An ideal solid is smooth, chemically homogeneous, rigid, insoluble and non-reactive. The CA is the angle between the solid surface and the tangent to the drop. The Gibbs energy of a drop on an ideal solid, as a function of all possible values of contact angles, has a single minimum. The Young CA is the one that is associated with the minimum in the Gibbs energy, namely with the equilibrium state of the drop.

However, ideal surfaces are very rare in practice. Usually, solid surfaces are at least somewhat rough and chemically heterogeneous. On rough surfaces, there are two regimes that need to be checked (please see **Fig. 4**: (1) the liquid penetrates the whole rough topography (Wenzel regime); and (2) the liquid penetrates the roughness only partially, and a stable air film separates between the solid and the liquid (Cassie-Baxter regime). The contact angle of the drop in the first regime was predicted by Wenzel to be (7)

$$\cos \theta_W = r_W \cos \theta_Y \quad (5)$$

where θ_W is the macroscopic, apparent CA, and r_W is the roughness ratio (ratio of true solid area to its projection). This equation predicts the CA to go down below θ_Y when $\theta_Y < 90^\circ$ and vice versa when $\theta_Y > 90^\circ$.

However, when the surface is hydrophobic, $\theta_{Y_{water}} > 90^\circ$, the situation may be different. Then, penetration of the roughness becomes expensive from a Gibbs energy point of view and the drop tends to penetrate only partially. It can also be stated that in the Wenzel regime, the solid-liquid contact area is increased by the complete penetration of the liquid. Thus, it appears that super-hydrophobicity is associated with partial penetration (7). This case was treated by Cassie and Baxter and their equation is (7).

$$\cos \theta_{CB} = r_f f \cos \theta_Y - (1 - f) = -1 + f(1 + r_f \cos \theta_Y) \quad (6)$$

where, f is the fraction of the projection area that projects a wetted solid area, and r_f is the roughness ratio of the wetted part of the solid. These observations have been known for a long time, but the phenomenon has not drawn much attention. However, the botanic observation (8) that leaves, especially of the Lotus flower, may be completely non-wettable, made this topic central in

many disciplines, as can be witnessed by the huge number of publications on it.

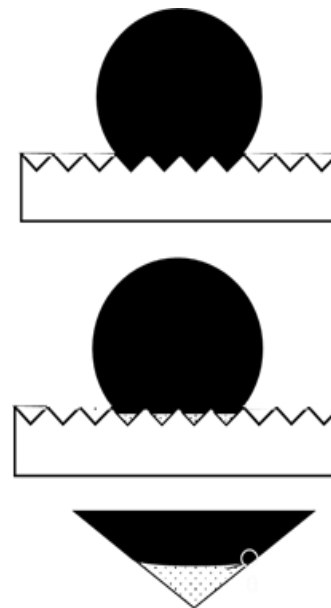


Fig. 4. The Wenzel regime (top) and the Cassie-Baxter regime (bottom).

The definition of super-hydrophobicity is not so straightforward, and is currently under study. However, from a practical point of view, a surface is considered super-hydrophobic if the CA of water on it is $>150^\circ$ and if the drop starts to move downwards when the surface is tilted by only a few degrees (referred to usually as roll-off angle). Analysis of Eq. 6 reveals interesting insight. As f becomes smaller (more air, less solid) the contribution of the first term on the right-hand side of Eq. 6 diminishes, but the effect of the second term increases. Values of r_f must practically between 1 and ~ 1.5 . Values of $\cos \theta_Y$ are between 0 and -0.3 (θ_Y from 90° to 120° , which is the highest in nature). Thus, $r_f \cos \theta_Y$ is between $\sim (0$ and $-0.45)$. With this analysis, $\cos \theta_{CB}$ is between -1 and $\sim (-1 + 0.55f)$. If we manage to make a surface that has $f = 0.25$, then θ_{CB} may be from 150° up. Thus, the goal appears achievable.

All of this was known to Cassie and Baxter already quite a few decades ago. But a question that has not been answered until recently is: does non-wettability depend only on average parameters, such as r_f or f ? By a simple mathematical analysis (9), we could show that for super-hydrophobicity to be stable, the geometry of the roughness must be convex. Otherwise, the Wenzel regime takes over.

While many scientists have been busy in looking for ways to produce non-wettable coating, other scientists have been trying to advance the possibility of similar phenomenon under different conditions. Two goals have been set: (1) super-hydrophobicity under water instead of in air; and (2) super-hydrophobicity, namely having high CAs with liquids other than water (**Hygro** is. It turns out, based on simple thermodynamic models, that

(1) super-hydrophobicity under water is possible under conditions that are quite like those in air (10); (2) Super-hydrophobicity is also possible, but there is a price to pay for it: the system is metastable, not stable (11). So, under all conditions, such a system may fall apart if there is some vigorous transfer of energy, such as environmental vibrations.

Conclusion and future perspectives

Simple mathematical analyses were used to elucidate essential theoretical bases of a few processes. In all cases that are presented above, the fundamental theory suggested clear indications for applied experiments. and practical production. Thus, they demonstrate the importance and truthfulness of the sayings of Feynman, Lewin, and Einstein.

All these case studies have old roots, but still have been amenable to additional theoretical analysis. So, I may end with a modest saying of myself: "There may not be anything new under the sun, but there is always a new way to look at it".

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