Effect of structured surface on contact angle using Sessile Droplet method

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Abstract. At the age of energy-crisis, enhancement of boiling heat transfer is the most crucial and advanced investigation field. Effects of surface characteristics, specially, surface wettability on pool boiling is yet to understand. Wetting, the ability of solid surface to reduce surface tension of a liquid in contact, can specify by measuring contact angle. Sessile drop method is a very sensitive process to measure contact angle, mainly used for evaluating, comparing and monitoring test surfaces. In this experimentation, a set of copper surfaces are roughened by emery grit size of 600, 1000, 1500 and 2000. Data on surface roughness (generated by AFM and FEG-SEM) and on dynamic contact angle (by macroscopic contact angle (CA) meter) are used to find relation between them. De-ionized water is used as working fluid to protect submerged secondary heater. In this experimentation, it is observed that advancing contact angle grows for surface roughened with higher emery grit-size.

1. Introduction
In our surroundings, everywhere in the nature, it can be observed that liquid encircles solid surface, and is most common natural phenomenon. This liquid encircling above the solid surface is known as Wetting. It is a kind of surface ability to trim its surface tension down. This can be noticed for a liquid in contact with it. In this era of innovation, it is very possible to detect test surface properties, especially by measuring contact angle. In literatures available in this field from the ages of Young to recent months, researchers are struggling to formulate the model to describe the inter-relation between surface wettability and contact angle [1, 2, 3, 4-8]. Papers are there amplifying contact angle from the end of surface roughness [9- 12]; some papers even discuss the possibilities of changing surface properties by forming thin film [13, 14] and in some papers effort to narrate surface roughness by wettability[15-18] is also visible. As a consequence, an opportunity, to expand a mathematical model for forecasting the test plane roughness, is growing.

Again, due to the above study, it is very evident that few effort was made to develop coorelation among liquid drop geometries, wettability and surface irregularity. Here, it is tried to scrutinize the dependency of contact angle on surface roughened by different grits of emery paper and other
geometric parameters. These parameters are associated with the drop which forms contact angle on surfaces roughened by different grit of emery. Intension of this work is to anticipate surface roughness and surface free energies when only data available is contact angle.

2. Substrate Characterization

2.1 Test surface preparation

Copper (C10800) is mainly used as tubing in refrigeration and air conditioning industries. Thus it is taken as experimental substrate due to its higher thermal and electrical conductivity, low cost. In figure 1, shape of the substrate is illustrated; it is cylindrical in shape with flat top and bottom. It has two step-wise sections; upper section is smaller in diameter than lower section. Dimension of the upper section is 9 mm × 1 mm and that of the lower section is 11 mm × 2 mm. For testing, end surface of upper section is used after surface modifications. Total four numbers of surfaces are used for this experiment; one each are polished by emery grit size of 600, 1000, 1500 and 2000 respectively. Then all surfaces are cleaned by acetone bath and rapped by tissue paper and kept with silica gel.

2.2 Surface Characterization

Two ways of characterizations, i.e., structural characterization and wettability characterization are applied for generation of data set.

2.2.1. Structural Characterization.

For measuring surface roughness for structured surface, AFM was conducted at Physics Department, NIT Agartala and related 1st set of AFM images were presented in a tabular form below:

| Grit Size | Roughness Parameter (R_a) |
|-----------|---------------------------|
| 600 grit  | 19.6 nm                   |
| 1000 grit | 20.9 nm                   |
| 1500 grit | 38.7 nm                   |
| 2000 grit | 51.0 nm                   |

Figure 2. 2D AFM Images for roughened surface by different emery paper
2.2.2. Wettability Characterization.
Water has been used as test fluid under sub-cooled condition at 20°C and atmospheric pressure with 45% RH. For measuring contact angle, Sessile drop method has been used. All trials are conducted on Microscopic Contact Angle Meter at IIT Patna. To generate contact angle profiles interface software FAMAS for Contact Angle measurement Format Version: 3.4 are used.

2.3. Computation
2.3.1. Anticipating Apparent Contact Angle (CA) and Surface Roughness.
It is known that for plain and ideal surface, surface free energy (SFE) operated in liquid -solid interface and angle formed by liquid with solid surface, has one relation as proposed by Young [19], which is,

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \]  

or,

\[ \gamma_s = \gamma_{sl} + \gamma_{l} \cos\theta \]  

2.3.2. Anticipating wettability of the surface from data of Dynamic CA.
It has been postulated that the investigational advancing contact angle can be the good estimate of the Young’s contact angle [20]. If result is H < 50°, test surface is homogeneous in nature; and, for H > 50°, test surface is of heterogeneous nature.
When in eqn. (2), \( \theta \) is replaced by \( \theta_a \), it will provide,

\[ \gamma_s = \gamma_{sl} + \gamma_{l} \cos\theta_a \]  

Then with the help of Chibowski [1, 2] correlation SFE of the solid surface can be determined, considering the value of surface tension of water at 20°C is \( \gamma_{lv} = \gamma_l = 72.8 \text{ mN/m} \) [21].
Using this value of \( \gamma_l \) in the eqn. 3, the value of \( \gamma_{sl} \) can find out. Smaller values of \( \gamma_{sl} \) indicate weaker SFE which indicates increasing wetting tendency.
In this present experiment, flat and solid surface is used. So, the wettability can be predicted by the Young–Dupre equation for the condition that neither \( \gamma_s \) nor \( \gamma_{sl} \) can be larger than the sum of other two surface energies. It imposes restriction due to which forecasting of complete wetting (when \( \gamma_s > \gamma_{sl} + \gamma_l \)) or zero wetting (when \( \gamma_{sl} > \gamma_s + \gamma_l \)) becomes possible. This wetting phenomenon can be measured both experimentally and numerically. ‘Affinity of the liquid for the solid’ is always opposed by the ‘friction between liquid molecules and solid molecules on the substrate’. This concept is used for measuring wetting phenomena. It is recognized as spreading coefficient and expressed as,

\[ S = \gamma_s - (\gamma_{sl} + \gamma_l) \]  

When \( S \) greater than 0, liquid spreads all over, complete wetting occurs; whereas, when \( S \) is less than 0, incomplete wetting occurs and well-defined contact angle formed.
As per the method described above, characteristics of test surfaces in trialling are anticipated and results tabled in Table no.1.

2.3.3. Determining wettability of the surface from Apparent CA.
As an equilibrium CA, apparent CA can be calculated macroscopically on solid surface of rough or heterogeneous nature. This parameter along with geometrical structure of substrates helps to calculate
the wetting of the substrate. Equilibrium condition can be reached with the spread of drop, displacing all air with liquid. According to Tadmor–Chibowski [22],

$$\theta_{ap} = \arccos \left( \frac{r_a \cos \theta_a + r_e \cos \theta_r}{r_a + r_e} \right)$$  \hspace{1cm} (4a)

Where, $r_a = \left( \frac{\sin^3 \theta_a}{2 - 3 \cos \theta_a + \cos^2 \theta_a} \right)^{\frac{1}{3}}$ and, $r_e = \left( \frac{\sin^3 \theta_a}{2 - 3 \cos \theta_e + \cos^2 \theta_e} \right)^{\frac{1}{3}}$

On real (rough or contaminated) surface, contact angle hysteresis is observed. So, local equilibrium contact angle may differ from point to point on surface [23].

2.3.4. Anticipating Surface Roughness Ratio ($r$).

With the augment of surface roughness, effective surface area increases [24]. When Wenzel state is considered,

$$\cos (\theta_{ap}) = r \cos (\theta_y) \quad [\text{valid for } r > 1]$$  \hspace{1cm} (5)

where, $\theta_{ap}$ is apparent contact angle; $r =$ [real rough surface area/ projected perfectly smooth surface]; and $(\theta_y)$ is the Young’s contact angle. But at $r = 1$, above relation becomes $\cos (\theta_{ap}) = \cos (\theta_y)$.

At the valley of the rough surface at the solid-liquid interface [25],

$$\cos \theta_{ap} = f_{LS} [\cos \theta_y + 1] - 1$$  \hspace{1cm} (6)

For real heterogeneous rough surface, it becomes necessary to combine eqn. (7) and eqn. (9)

$$\cos \theta_{ap} = \frac{r_{LS} f_{LS}}{[\cos \theta_y + 1] - 1}$$  \hspace{1cm} (7)

Now, using the correlation presented by Whyman et al. [22], and putting values of $\theta_{ap}$, $\theta_y$, and $\theta_{LS}$, surface roughness ratio ($r$) can be anticipated.

But, using values obtained from AFM data, Surface roughness ratio ($r_{AFM}$) can be defined and as shown in Table 1.

| Advancing CA | Receding CA | Advancing CA | Receding CA |
|--------------|-------------|--------------|-------------|
| Surface Roughened by 600 grit emery | $\theta_a = 107.0^\circ$ | $\theta_r = 16.7^\circ$ | $\theta_a = 100.1^\circ$ | $\theta_r = 19.6^\circ$ |
| Surface Roughened by 1500 grit emery | $\theta_a = 87.6^\circ$ | $\theta_r = 20.9^\circ$ | $\theta_a = 95.3^\circ$ | $\theta_r = 22.4^\circ$ |

**Figure 3:** Advancing and receding angle for respective surfaces ‘roughened by different grit of emery’. (Images are from CA meter)

2.4. Uncertainty while measuring Dynamic Contact Angle

For Contact angle Meter, uncertainty of the dynamic contact angle is approximated as $\pm 1^\circ$. For emery roughened surface, percent uncertainty of surfaces is smaller (less than 1%). As uncertainty are
calculated 3.72% of the experimental values, within the tolerable range of ± 5%, making the data set acceptable [26].

3. Result and Discussion
Presently surface roughness ration $\text{R}$ is calculated using Young – Laplace Model on assumption that surfaces are homogeneous perfectly flat and smooth; and the liquid used is pure. But in experiments, cases are not real. There are heterogeneity in the surfaces and liquid used are not 100% pure.

| Table 1: Calculating roughness of test surface roughened by emery paper. |
|---------------------------------------------------------------|
| Copper Surface                | Treated surface by emery grit size |
|                               | 600  | 1000 | 1500 | 2000 |
| $\Theta_a$ (°)                | 107.00 | 100.10 | 87.60 | 95.30 |
| $\Theta_r$ (°)                | 16.70  | 19.60  | 20.90 | 22.40 |
| Hysteresis (H)                | 90.30  | 80.50  | 66.70 | 72.90 |
| Anticipated SFE on solid surface $\gamma_s$ [mN/m]           | 12.30  | 14.32  | 14.73 | 12.50 |
| Anticipated SFE on solid-liquid interface $\gamma_{sl}$ [mN/m]| 25.70  | 15.72  | 9.40  | 24.77 |
| Anticipated Apparent CA ($\theta_{ap\ predicted}$)           | 49.27  | 49.01  | 51.05 | 57.41 |
| Mean Apparent CA ($\theta_{ap\ mean}$)                       | 61.85  | 59.85  | 54.25 | 58.85 |
| $r_p$ derived from mean apparent CA                            | 0.83   | 0.85   | 0.84  | 0.79  |
| $r_p$ by AFM data                                              | 0.80   | 0.75   | 0.83  | 0.77  |

Relations among different parameters for each surfaces acquired from Contact Angle Meter are plotted below in a tabular form.
In figure 4, for test surface roughened by emery grit 600, 1000, 1500 and 2000, has been depicted separately by figure 4a to figure 4d respectively. Graphs are analyzed and presented below in a tabular form:

| Emery grit size | 600 | 1000 | 1500 | 2000 |
|-----------------|-----|------|------|------|
| CA At 0 sec. | CA 100° | CA 93° | CA 107° | CA 95° |
| After 20 sec. | CA 0° | Linearly decreasing. | Linearly decreasing. | Linearly decreasing. |
| Volume (same volⁿ, In each drop) | Max. vol. at 3 sec. | Max. vol. at 2.5 sec. | Max. vol. at 3.5 sec. | Max. vol. at 3.5 sec. |
| Linearly diminishes to 0mL at 20 sec. | Linearly diminishes to 0mL at 16 sec. | Linearly diminishes to 0mL at 35 sec. | Linearly diminishes to 0mL at 25 sec. |
| Radius Max radius at 3 sec. | Max radius at 2.5 sec. | Max radius at 2.5 sec. | Max radius at 4.5 sec. |
| Retain the radius upto 16 sec. | Retain the radius upto 15 sec. | Retain the radius upto 25 sec. | Retain the radius upto 17.5 sec. |
| Sharp drop to 0 at 20 sec. | Sharp drop to 0 at 25 sec. | gradually drop to 0 at 35 sec. | step-wise dropped to 0 at 25 sec. |
| Remarks | It is wettable and suitable for heat transfer applications. | Though other two parameters reach to zero level, but CA never touches to zero. Surfaces showing hydrophobic nature. Not suitable for heat transfer applications. | It is wettable and best than other surface under test as it provides 5sec extra time to carry heat. |

In simple line, these trends are also supported by the table 1. The observed values of calculated surface roughness shown in table 1 are different from the surface roughness measured directly by the Atomic Force Microscopy for the test surface with cross section of 5µm X 5µm. Here, it is also noticed that SFE in solid surface is lowest for surface roughened by the emery 2000.
4. Conclusion

According to the result and discussion, it can be pointed that liquid-volume present in the drop, drop-radius, contact angle and time are inter-related. Surface roughened by emery grit 2000 is most wettable than other roughened surface under present experimental condition. Surface roughness shows growing trend with rising emery grit-size. Further, it is also noticed that with the rise of surface roughness, contact angle also augmented. Similar trends for all parameters observed in graphs for surfaces roughened by 600, 1000, 1500 and 2000 emery.

References

[1] Chibowski, E., Ontiveros-Ortega, A., Perea-Carpio R., 2002, J. Adhesion Science and Technology, 16 1367-1404
[2] Chibowski, E., 2003, Advances in Colloid and Interface Science, 103 149-172.
[3] Rishi Raj, Enright, R., Zhu, Y., Adera, S., and Wang, E. N., 2012 ‘Unified Model for Contact Angle Hysteresis on Heterogeneous and Superhydrophobic Surfaces’, J. Langmuir 28 15777 – 15788.
[4] Gao, L., and McCarthy, T.J., How Wenzel and Cassie were wrong, 2007, Langmuir 23 3762–3765.
[5] Munshi, A. M., Singh, V. N., Kumar, M, and Singha, J. P., 2008 Effect of nanoparticle size on sessile droplet contact angle, J. of Applied Physics 084315 103-107.
[6] Cansoy, CE, Erbil, HY, Akar, O, and Akin, T, 2011 Effect of pattern size and geometry on the use of Cassie–Baxter equation for superhydrophobic surfaces, Colloids Surf. A - Physicochem. Eng. Aspects 386 116-124.
[7] Yi, Z D, Wei, Q, and Deng, W L., 2011 Hydrophobic mechanism and criterion of lotus-leaf-like micro-convex-concave surface, Chinese Science Bulletin 56 1623–1628.
[8] Bottiglione, F., and Carbone, G., 2015 An effective medium approach to predict the apparent contact angle of drops on super-hydrophobic randomly rough surfaces, J. of Physics: Condensed Matter 27 015009 – 015018.
[9] Hong, K. T., Imadojemu, H., and Webb, R. L., 1994 Effects of Oxidation and Surface Roughness on Contact Angle, Experimental Thermal and Fluid Science 8 279-285.
[10] Erbil, H.Y., McHale, G., Rowan, S.M., and Newton, M.I., 1999 Determination of the receding contact angle of sessile drops on polymer surfaces by evaporation, Langmuir 15 7378-7385.
[11] Extrand, C.W., 2003 Contact angles and hysteresis on surfaces with chemically heterogeneous islands, Langmuir, 19 3793–3896.
[12] Zhou, C. X., Yuan, X.G., Fan, L. T., Zeng, A. W., Yu, K.T., Kalbassi, M., and Porter, K. E., 2010 Experimental study on contact angle of ethanol and N-propanol aqueous solutions on metal surfaces, Distillation Absorption 359-364.
[13] Deshmukh, S.G., Kheraj, V., Karande, K.J., Panchal, A.K., and Deshmukh, R. S., 2019, Hierarchical flower-like Cu3BiS5 thin film synthesis with non-vacuum chemical bath deposition technique, Materials Research Express 6 084013.
[14] Deshmukh, S.G., Kheraj, V., and Panchal, A.K., 2017, Development of Cu3BiS5 thin films by chemical bath deposition route, J. of material science: Materials in Electronics, 28 11926-11933.
[15] Wenzel, R.N, 1936 Resistance of solid surfaces to wetting by water, Industrial and engineering chemistry 28 988.
[16] Quere, D., 2002 Rough ideas on wetting, Physica A 313 32 – 46.
[17] Quere, D., 2008 Wetting and Roughness, The Annual Review of Materials Research 38 71–99.
[18] Kubiak, K.J., Wilson, M.C.T., Mathia T.G., and Carval, 2011, Wettability versus roughness of engineering surfaces, Wear 271 523–528.
[19] Young, T., An essay on the cohesion of fluids, Philosophical Transactions of the Royal Society of London, 95 65-87.
[20] Kwok, Y., 1998 J. of Colloid and Interface Science, 206 44-51.
[21] Carey, V P, 1992 Liquid – Vapour phase change phenomena, Hemisphere Pub. Corp., Ed. 1st, Chapter - 3 57-76
[22] Whyman, G., Bormashenko, E., and Stein, T., 2008 The rigorous derivation of Young, Cassie–Baxter and Wenzel equations and the analysis of the contact angle hysteresis phenomenon, Chemical Physics Letters (Elsevier) 4503 55–59.
[23] Nishino, T., Meguro, M., Nakamae, K., Matsushita, M., Ueda, Y., 1999 Langmuir 15, 4321-4323.
[24] Wenzel, R.N., 1936 Resistance of solid surfaces to wetting by water, Ind. Eng. Chem 28 988-994.
[25] Cassie, A.B.D., and Baxter, S., 1944 Wettability of porous surfaces, Trans. Faraday Soc. 40 546-551.
[26] Deshmukh, S.G., Patel, S.J., Patel, K.K., Panchal, A.K., and Kheraj, V., 2017, Effect of Annealing Temperature on Flowerlike Cu3BiS3 Thin Films grown by Chemical Bath Deposition, Journal of Electronic Materials, 46 (10) 5582-5588.