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Different Competitive Growth Model for Finite Size Scaling Study of Rough Surfaces: A Smart Approach for Estimating Hydrophobicity

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***Abstract*—Rough surface has been produced by simulation in 1+1 dimension following different competitive growth models namely random deposition with ballistic deposition and random deposition with surface relaxation with ballistic deposition and calculated the corresponding scaling exponent. It is seen that though the nature of the interface evolution follows the well-established Edwards-Wilkinson growth model or Kardar–Parisi–Zhang model but the values of corresponding scaling exponents do not match exactly with the existing literature. Further it has been seen that the system does not switch over from growth region to saturation region suddenly after a single critical time as has been suggested by the existing theories but there are two distinct crossover regions where the system shows different scaling property.**
This theoretical finding has been coupled with existing Cassie-Baxter equation to relate the evolved roughness with hydrophobic response of the surface. In this regard, quantitative expression of the water contact angle based on simple assumptions has been represented.

Keywords- Scaling, discrete models for surface growth, Ballistic phenomena, Roughness, Hydrophobicity

I. INTRODUCTION

In the last few decades, considerable efforts have been put for detail understanding of different growth models that results rough surfaces by different specific ways [1, 2]. Also with development of different microscopic techniques namely atomic force microscopy people now, are trying to create a link between the experimental results and theoretical studies. Basically there are two kinds of approaches for studying these kinds of growths in d dimensional spaces; one approach includes discrete growth models that are developed by setting of certain deposition obeying either nearest neighbour interaction or next nearest neighbour interaction or others. It is seen that those specific rules can adequately describe the temporal and spatial evolution of the growing surfaces. The entire concept of this discrete model can be best designated by the most well-known Family-Vicsek phenomenological scaling law [3].There are numbers of different discrete models falling different universality class that people use to describe spatial and temporal evolution of a growing rough surface. Some examples are random deposition (RD), random deposition with surface relaxation (RDSR), solid on solid model (SOS), body centred solid on solid model (BCSOS), ballistic deposition (BD) [4-6] and many others. Also as the main aim of all these models are to best describe different natural phenomena people are developing models called competitive growth where it is considered that a definite growth is taking place with a specific probabilities say p whereas the other with probability (1-p) [7, 8]. Thus a more realistic surface can be obtained here.

In the second approach different continuum equation is proposed that may be both linear and nonlinear class. For example Edwards-Wilkinson model (ED) or model suggested by Kardar–Parisi–Zhang (KPZ).

As has been previously mentioned different discrete growth model are defined by different deposition rules so it is very obvious that there should exist some definite equations called scaling equation that describe the system. These scaling equations may fall within KPZ universality class or ED class or something others. So it is itself a challenging task to recognize a certain growth profiles in which class it is belonging to. This can be done by calculating different exponents of the corresponding equation called scaling exponent.

There are numbers of works that have been done regarding the determination of scaling exponent of different universality classes and nature of surface or roughness evolution. These works include both1+1 or 2+1 dimension with like particles or particles with different shapes and sizes obeying certain growth mechanism or some competitive growth models [9]. Even after all these reports, so far the author is concern there are not much efforts to build a bridge between these kind of theoretical simulation with some definite properties of the system. The properties include electrical transport, propagation of cracks through the media porosity and many others. Motivated by above mentioned literature study, here two kinds of competitive growth model RD-BD (model 1) and RDSR-BD (model 2) have been simulated in 1+1 dimension considering a single type particles. The corresponding scaling exponent has been calculated and tabulated for different system sizes. Also the porosity of the produced surface has been calculated and Cassie-Baxter equation has been utilized in order to have quantitative ideas about the contact angle of water on this surface. Though the calculation is not adequately giving the exact values of water contact angle but it surely gives the variation of water contact angle with the fractional change of the deposition nature for both the models. Also the original results are supposed to be deviated from the theoretical data by a constant factor only.

The paper is organized as follows. In section 2, a brief description of the existing discrete growth models with mathematical equation is given. Also the basic assumption and condition of the model is depicted here. Section 3, describe the results that are obtained followed by its relevance with Cassie-Baxter equation of hydrophobic. Finally, in section 4, the conclusions are drawn from the numerical results described in previous sections.

II. MODELING AND SIMULATION

The roughness of a growing surface can be characterized in terms of w(t) which is defined as:

$$w(L,t) = \sqrt{\frac{1}{L}\sum_{i=1}^{L}(h(i,t) - H(t))^2} \quad (1)$$

Where L is the system size h(i,t) is the height of the i^{th} site at time t and H(t) is the mean height of the surface given by:

$$H = \frac{1}{L}\sum_{i=1}^{L} h(i,t) \quad (2)$$

The basic conditions of three different models are rather simple and schematically shown in **Fig. 1.** In all the three cases at any instant t we randomly choose a certain site i having h(i) and release a small particle. In case of RD the particle falls and sticks exactly to the position it was released upon thus increasing its height by one unit, In the second case i.e. in RDSR model the particle so chosen falls on the i^{th} site but can be relaxed to its nearest neighbour if the height of the neighbour is lesser. Thus In case of BD the randomly chosen particle can stick to the nearest neighbour site where it finds the height is the maximum.

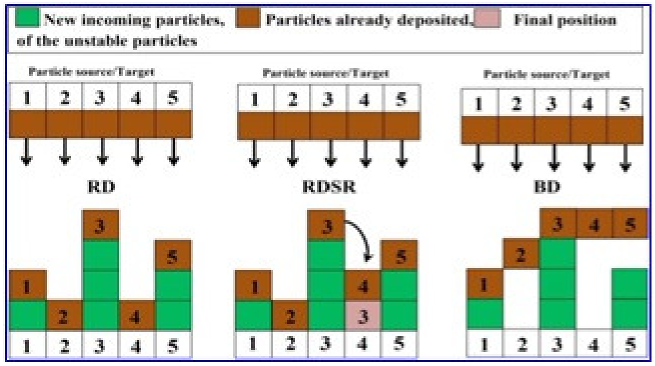

Fig.1: Schematics, represents the basic definition of three kinds of growth processes

Thus the basic difference between RD and the other two models is that in former case the surface does not have any correlation and thus w(t) ∞ t. Thus interface width can continuously increases with time. In the other two models as particles can be relaxed into the neighbouring sites or can choose a favourable position, a surface correlation grows and here w(t) cannot increase endlessly with time and saturation comes after a certain time t_x called critical time.

The scaling behaviour changes here in two time regime i.e. $t < t_x$ and $t > t_x$. In two regimes the scaling relation takes the following form:

$$W(L,t) \sim t^{\beta}[t \ll t_x] \qquad (3a)$$

$$w_{sat}(L) \sim L^{\alpha}[t \gg t_x] \qquad (3b)$$

$$\text{with} \qquad t_x \sim L^{z}\left[z = \frac{\alpha}{\beta}\right] \qquad (3c)$$

Here α, ß and z are respectively called the roughness, growth and dynamic exponent having specific values depending upon in which universality class the system belongs to. In case of RD model, as there is no correlation, the system has only one exponent ß. The above three relation can be summarized in a single expression runs as

$$w(L,t) \sim L^{\alpha} f\left(\frac{t}{L^{z}}\right) \qquad (4)$$

It is to be noted that though both RDSR and BD consider correlation the values of some exponents are different. The reason is that RDSR model falls into the linear universality class whereas the BD falls into the nonlinear KPZ class. The basic continuum growth equation for the two systems is respectively as follows:

$$\frac{\partial h(x,t)}{\partial t} = G[h(x,t)] + \eta(x,t) \qquad (5)$$

where G[h(x, t)] is the deterministic growth time and η is the noise term. ED class G is written as $G[h(x, t)] = \nu\nabla^2 h$ following Edward-Wilkinson equation [10] whereas KPZ class introduced nonlinear term into G and wrote $G[h(x, t)] = \nu\nabla^2 h + (\lambda/2)\nabla h^2$.The first term on the right hand side describes the relaxation of the interface caused by a surface tension v, and the second term reflects the presence of lateral growth with the coefficient λ.

In this work we have studied two competitive models for two different system sizes. In first process competition is made between RD and BD having assumption that if one process occurs with probability p then other would occur with that of (1-p). For second case same has been done with RD process being replaced by RDSR. It is assumed that particle generator and surface were identical in size and thus no particle was wasted. The simulation was made running until saturation comes. It was also assumed that in each unit time the numbers of particles generated were exactly equal to the numbers of sites they were allowed to fall upon and thus the ratio of site numbers and particle numbers were always remained constant and equal to the time duration.

III. RESULTS

Fig.2 a and b show the log-log plots of w with t for two different system sizes L = 50, 400 and for different values of p when system follows RD-BD competitive model. Here p = 0 signifies the system follows pure RD models and corresponding log(w) - log(t) plot has been shown inset of **Fig.2** b. It is seen from **Fig.2** that in all the case (except for p = 0) log[w(t)] 1st growing with times and after a certain crossover time it tends to get saturated.

This is general nature of this kind of surface evolution. The new thing that can be observed here is before saturation region the slope of the curves does not carry an unique value and so instead of one two distinct crossover region can be observed where the linear rise of log[w(t)] shows two distinct slopes.

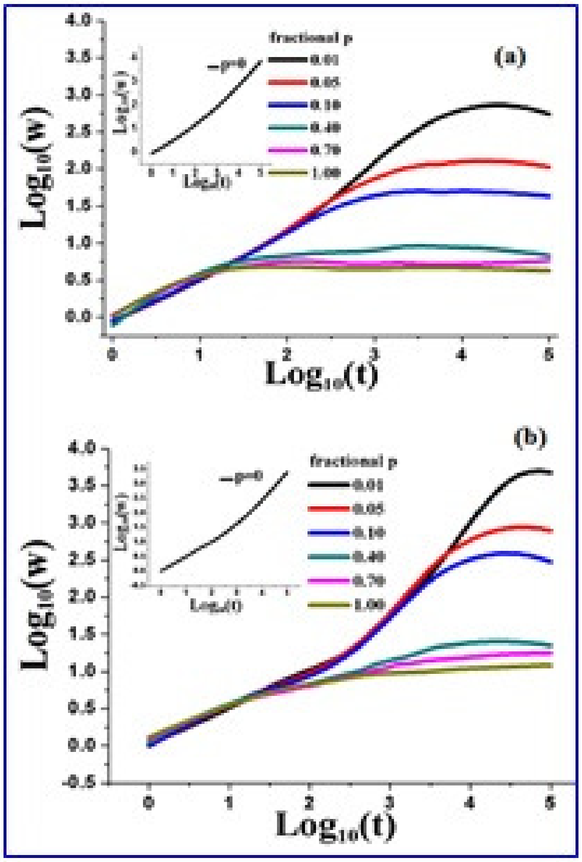

Fig.2: Log-Log variation of interface width with time for a system undergoing RD-BD models; (a) L = 50 and (b) L = 400; (Inset the same for p = 0).

Table I summarizes the values of critical times and the slope of each parts as well as total slope of every linear plots corresponding to each L and p. It is seen that both the critical time t_{x1} and t_{x2} decreases as the system follows more and more ballistic model. The values of growth exponent also follows the same scaling law but the values of m not being matched with any existing reports suggesting some other scaling equation may be needed to describe the growth of system uniquely.

Fig.3 shows variation of w with p for both the system size and it can be seen that w decreases with increasing p, at first rapidly and then with much slower rates. This is expected since the increase in p means the system more and more goes into ballistic nature and thus a new particle has enough probability to position it globally and thus the roughness gets saturate more easily with much lower values.

A repetitive simulation has been done assuming that the system is going second competitive growth model between RDSR and BD. **Fig.4, 5** and **Table II** shows corresponding results extracted out of the simulation.

Fig.4 a and b shows the log-log plots of w with t for two different system sizes L = 50, 400 and for different values of p when system follows RDSR-BD competitive model and like the previous case p = 0 signifies the system follows pure RDSR models.

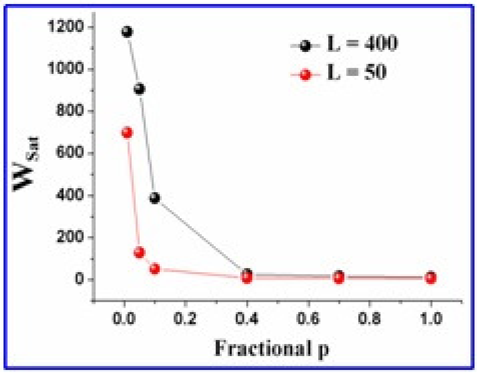

Fig.3: Variation of W_{sat} with p for the system undergoing RD-BD models

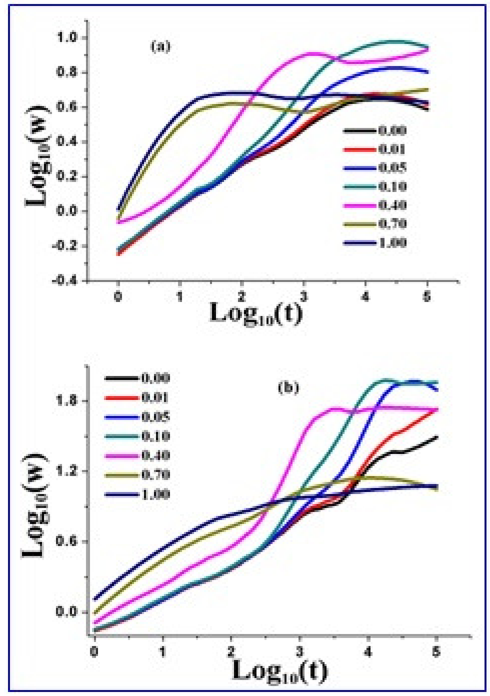

Fig.4: Log-Log variation of interface width with time for a system undergoing RDSR-BD models; (a, b) L = 50 and (c, d) L = 400

It is to be noted here that as summarized in **Table II** and also that can be seen from **Fig.5** that unlike the previous case the saturation roughness values do not varies monotonically and it first shows a steep increase and then a decrease followed by subsequent saturation effect.

Table I: The values of critical times, slopes of different regions obtained from log-log plots of w with t and values log(W_{sat}) values for the system undergoing RD-BD model

L = 50, T = 10^5						
p	**$Log_{10}t_{x1}$**	**$Log_{10}t_{x2}$**	**m_1**	**m_2**	**m**	**$Log_{10}(W_{sat})$**
0.00	2.54	--------	0.633	0.945	0.778	-------
0.01	1.953	3.766	0.603	0.917	0.752	2.844
0.05	1.599	3.182	0.659	0689	0.669	2.108
0.10	1.478	2.854	0.598	0.607	0.598	1.709
0.40	0.737	1.672	0.757	0.356	0.544	0.889
0.70	0.724	1.661	0.578	0.307	0.413	0.766
1.00	0.554	1.283	0.663	0.386	0.497	0.673
L = 400, T = 10^5						
p	**$Log_{10}t_{x1}$**	**$Log_{10}t_{x2}$**	**m_1**	**m_2**	**m**	**$Log_{10}(W_{sat})$**
0.00	3.035	---------	0.519	0.887	0.657	-------
0.01	2.768	4.533	0.511	1.246	0.762	3.071
0.05	2.54	3.92	0.490	1.053	0.676	2.957
0.10	2.46	3.814	0.461	0.938	0.612	2.589
0.40	1.312	3.79	0.487	0.291	0.326	1.408
0.70	1.077	3.644	0.451	0.239	0.286	1.222
1.00	1.283	3.054	0.413	0.192	0.291	1.054

Fig.5 shows it with more profound effect. The magnitude of the roughness is much lesser in case of second competitive models for all values of p and L. This is rather expected since in case of RD the surface never shows

any saturation effect whereas both BD and RDSR techniques are associated with a saturation phenomenon. The values of both t_{x1} and t_{x2} both decreases with increasing value of p suggesting that ballistic nature helps the system to get saturated more rapidly.

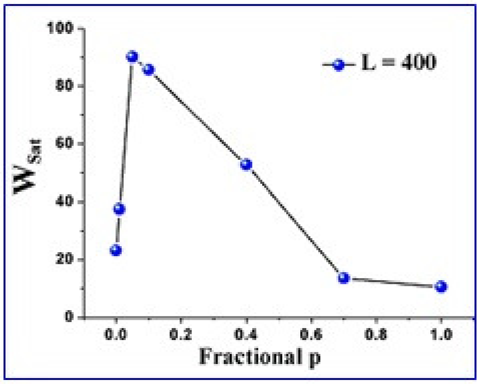

Fig.5: Variation of W_{sat} with p for the system undergoing RDSR -BD models (L = 400)

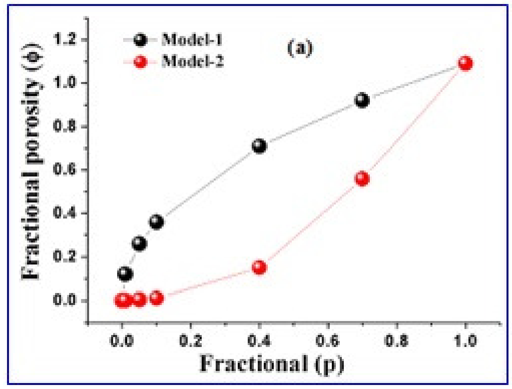

Fig.6: Variation of fractional porosity of the system undergoing RD-BD and RDSR-BD process (L = 400)

Here also the scaling exponent, especially the value of growth exponent, does not totally match with any of the existing values (1/2 for RD or RDSR and 1/3 for BD). But still the considering the entire growth region β values tend to coincide with that expected from BD model.

Porosity of the system has also been estimated from the simulation results. Here porosity (ϕ) has been defined as $\phi = N_v/N_t$ where N_v is the number of void site and N_t is total site, i.e. if N_f be the number of filled site then $N_t = N_v + N_f$. It is to be noted that as except BD model other two models correspond to finding the site of lowest height by newly arriving particles there is no question of porosity for them and hence ϕ is associated with BD model only.

Fig.6 shows the variation of fractional porosity for the system being grown with two competitive growth model with different values of p for L = 400. It can be seen that for all values of p except 0 and 1 the porosity of the RD-BD system is much better than that associated with RDSR-BD models.

At 0 and 1 values of p the value of ϕ coincides for two models which is very much expected since p = 0 signifies the system undergoes pure RD or RDSR model in which the concept of porosity does not come. When p = 1 the system comes to purely BD mode where the porosity should not depend upon the system size but the deposition process so the numerical values of ϕ comes out to be the same.

Table II: The values of critical times, slopes of different regions obtained from log-log plots of w with t and values log(W_{sat}) values for the system undergoing RD-BD model

L = 50, T = 10^5						
p	**$Log_{10}t_{x1}$**	**$Log_{10}t_{x2}$**	**m_1**	**m_2**	**m**	**$Log_{10}(W_{sat})$**
0.00	1.149	3.705	0.275	0.219	0.231	0.642
0.01	1.132	3.814	0.275	0.227	0.237	0.68
0.05	0.782	4.277	0.257	0.266	0.261	0.834
0.10	0.846	3.827	0.276	0.334	0.313	0.981
0.40	0.968	2.658	0.211	0.443	0.366	0.886
0.70	0.529	1.433	0.614	0.348	0.455	0.662
1.00	0.481	1.223	0.663	0.386	0.497	0.664
L = 400, T = 10^5						
p	**$Log_{10}t_{x1}$**	**$Log_{10}t_{x2}$**	**m_1**	**m_2**	**m**	**$Log_{10}(W_{sat})$**
0.00	2.111	4.289	0.274	0.419	0.349	1.365
0.01	2.525	4.386	0.288	0.488	0.373	1.574

0.05	2.342	4.367	0.277	0.701	0.444	1.955
0.10	2.379	4.094	0.282	0.863	0.496	1.933
0.40	2.391	3.212	0.331	1.102	0.481	1.722
0.70	1.004	3.341	0.457	0.276	0.312	1.132
1.00	1.004	2.573	0.429	0.236	0.318	1.02

The concept of porosity plays an important role in determining the hydrophobic nature of the surface and quantitative determination of the water contact angle. On a hydrophobic surface, water has a very large contact angle and also it can roll off very easily i.e. it shows very low hysteresis (for systems in Cassie equilibium state) [11]. Here a drop sits on the top of the asperities of the surface and water cannot penetrate into the gap. There is another kind of system called Wenzel state [11] where in spite of large contact angle the system shows a large hysteresis i.e. the water doesn't roll off easily. Here water can penetrate into the cavity. **Fig.7** a, explains the both the equilibrium conditions schematically.

The equations that describes the Cassie state runs as

$$\mathrm{Cos}(\theta) = \sigma\mathrm{Cos}(\theta_1) + (1-\sigma)\mathrm{Cos}(\theta_2) \quad (6a)$$

It is to be noted that Wenzel state is rare to observe in real world as it requires a perfect homogeneous system which is not expected in case of a competitive growth model. Thus we have taken **equation 6**a to describe the system. We assume the substrate to be cleaned silicon on whom when smooth carbon film is deposited the value of θ_1 comes out to be ~ 40^o. Now as stated earlier σ = (top pillar surface)/(projected surface) that should vary inversely with W_{sat} and thus $\sigma \propto 1/W_{sat}$. Again for our substrates "σ" can be expressed with geometrical parameters:

$$\sigma = (A/p^2) \times S \quad (7)$$

where S is the pillar surface and A: geometrical disposition factor giving the number of pillars per area, for square disposition A = 4 × ¼ = 1 and for linear deposition A = 2 × ½

where θ is the contact angle (experimentally measured), θ_1 is the contact angle of water on a flat surface of the material under investigation and $\theta_2 = 180^o$ is the contact angle of water on air. $\sigma$is the solid fraction of surface area at the top of the asperities and hence$\phi = (1-\sigma)$ would represent the surface porosity.

For a ridges of height h, width d and periodicity P, the expression for σ would be $\sigma = d/P$ (**Fig.7** b). For the Wenzel state the equilibrium equation is rather simple and just runs as

$$\mathrm{Cos}(\theta) = \eta\mathrm{Cos}(\theta_1) \quad (6b)$$

Here η is the ratio between real surface areas to projected surface area.

It is to be noted that Wenzel state is rare to observe in real world as it requires a perfect homogeneous system which is not expected in case of a competitive growth model.

Thus we have taken **equation 6**a to describe the system.

In our case we have assumed a cubic particle of unit dimension is being deposited thus in our case P = S = A = h = 1. This immediately gives $P = a\times(W_{sat})^{0.5}$, where a is proportionality constant. Generally it is found from any calibrated data in order to have the exact inter-columnar distance but for this time being we take a, to be unity in order to find the variation of inter-columnar distance with fractional position of BD to take place. The variations for both the models with both the system sizes have been shown in **Fig.8.** It has been seen that the variation as expected varies with p, in the same manner as that of W_{sat} for both the competitive models and for both the system sizes. This also helps in determining quantitative values of contact angle. The variation has been shown in **Fig.9.** It has been seen that in case of model 1 i.e. RD-BD model with increasing p the water contact angle reduces from ~ 176 to ~ 126 ^{o} whereas for RDSR-BD model it does not follow any monotonic pattern but stays within the value ~157 – 128 ^{o}. The first conclusion that can be drawn from here is that in each case the increasing value of p seems less favours the hydrophobicity of the system which means that roughness of the system plays the key role to determine the hydrophobic nature in the Cassie state. The results show that the water contact angle for a specific system depends on the system size, which is somewhat unusual for real systems. This may be due to the fact that the water contact angle not only solely depends upon the roughness of the surface but highly sensitive to the surface chemistry also. So decrease of system size may change the surface chemistry in such a way that overall effect towards the water repellency of the surface remains constant. This has to be investigated further. The greater water contact angle of water droplet on the surface grown under RD-BD model than RDSR-BD can again be explained in terms of the enhanced roughness of the 1st system as in case of RD model the roughness can vary indefinitely thus giving better hydrophobicity of the corresponding system.

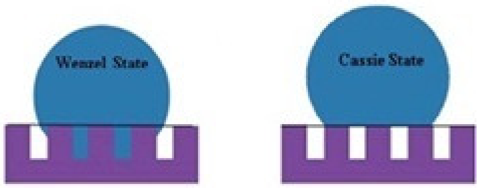

Fig.7: (a) Schematic, showing Wenzel state and Cassie equilibrium state

Fig.7: (b) Schematic of the substrate showing the inter-Columnar distance

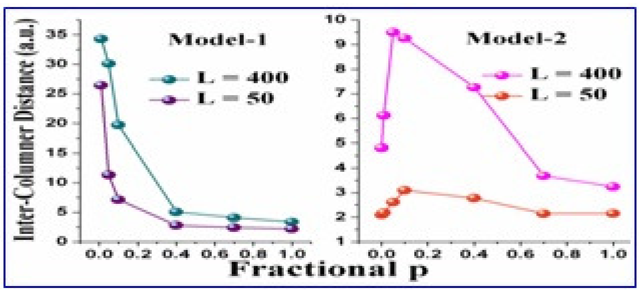

Fig.8: Variation ofinter-columnar distance with fractional values of p for both the models and both the values of L

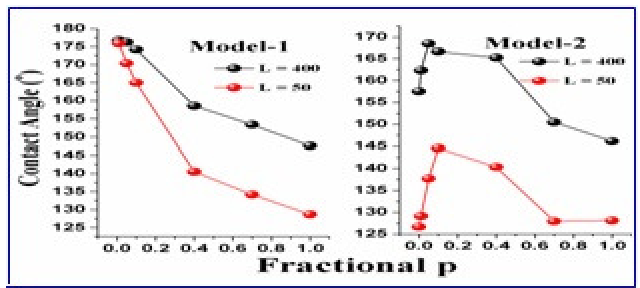

Fig.9: Variation water contact angle with fractional values of p for both the models and both the values of L

I. CONCLUSIONS

This work reports a comparative simulation study of time evolution of a rough surface generated by two different competitive growth mechanism namely random deposition-ballistic deposition, and random deposition with surface relaxation and ballistic deposition model. It has been found that the growth cannot be described by any existing scaling relation uniquely thus losing its universality. There exists in case of both the models three distinct growth regime separated by two critical time. Three regimes behave differently being described by different scaling relation. The saturation roughness has been found to be decreased with increasing ballistic nature in case of RD-BD model whereas it does not follow any definite nature in case of other model. Porosity as well as inter-columnar distance has been calculated based on simple assumption. The water contact angle has also been quantitatively calculated here from and it has been seen that water contact angle decrease with increasing ballistic nature of the deposition. The variation of water contact angle with surface roughness has been quantitatively verified in case of Cassie state. This systematic study would definitely help the researchers to draw a relation between deposition process and water repellent behaviour of the system.

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