Kinetic roughening of aggregates of patchy colloids with strong and weak bonds

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Abstract – We study the irreversible aggregation of films of patchy spherical colloids with directional and selective interactions. We report a crossover of the interfacial roughening from the Kardar-Parisi-Zhang (KPZ) to the KPZ with quenched disorder (KPZQ) universality class when the difference between the strong and weak bonds is sufficiently large. We calculate the critical exponents and identify the crossover between the two regimes.

Introduction. – A very active field, in soft matter, is the experimental and theoretical study of the nonequilibrium scaling of growing interfaces [1–15]. In particular, recent work on the aggregation of colloids at the edge of an evaporating drop, revealed that the interfacial roughening depends on the asymmetry of the colloidal shape. The experimental results suggest a Poisson-like growth for spherical colloids while for strongly anisotropic colloids the growth is in the universality class of Kardar-Parisi-Zhang with quenched disorder (KPZQ). For moderate anisotropy the classical Kardar-Parisi-Zhang (KPZ) universality class is observed [16–18]. Here, we consider the asymmetry of spherical colloids by including regions on the colloidal surface with anisotropic interactions (patches).

The Kardar-Parisi-Zhang (KPZ) is a very robust universality that describes successfully many growing interfaces [19]. Underlying this class is the stochastic differential equation,

$$\frac{\partial h(x,t)}{\partial t} = \nu \frac{\partial^2 h(x,t)}{\partial x^2} + \lambda \left( \frac{\partial h(x,t)}{\partial x} \right)^2 + \eta(x,t),$$

(1)

where $h(x,t)$ is the height of the interface at the lateral position $x$ and time $t$. The first term on the right-hand side is the interface relaxation due to surface tension $\nu$ and the nonlinear term accounts for lateral growth [20]. The noise term $\eta(x,t)$ has zero average. If the noise does not depend on time (quenched noise) but on the lateral position and height, $\eta(x,h)$, the growth falls into another universality class, the KPZ with quenched disorder (KPZQ) [20–22]. This class can be described by the differential equation,

$$\frac{\partial h(x,t)}{\partial t} = \nu \frac{\partial^2 h(x,t)}{\partial x^2} + \lambda \left( \frac{\partial h(x,t)}{\partial x} \right)^2 + F + \eta(x,h).$$

(2)

Here a constant driving force $F$ must be included to keep the interface from pinning when $\eta(x,h) < 0$.

The last two decades have been fruitful on models and experimental setups developed to shed light on the KPZ universality with quenched disorder [21,23–29]. From these studies, two main results emerged: First, below a critical driving force, the interface is pinned and above it depinned. Second, the scaling of the interface above the critical driving force, is initially in the KPZQ class but it does cross over to the KPZ class for sufficiently large length and/or long time scales. Solely at the critical driving force is KPZQ observed, in the thermodynamic limit.

The new ingredient in our study is the use of colloids with anisotropic regions distributed on their surface (patches) yielding highly directional pairwise interactions. This type of colloids, called patchy colloids, can be synthesized using many different techniques [30–37]. Along the experimental advances, significant progress has been made theoretically. However, theoretical understanding has been focused mostly on the study of equilibrium phase diagrams [38–41]. More recently, the kinetics of aggregation [42,43] and self-organization on substrates was addressed [44–49], and the nonequilibrium adsorption revealed interesting behavior for single-type colloids [45],
mixtures of colloids [46], or colloids with selective interactions [47].

Patchy colloids with distinct patch-patch interactions yield interesting properties in the bulk, such as a vanishing critical point [50,51] as well as unusual thermodynamic and percolation properties [52,53]. Usually, 2A colloids are considered, with strong A- and weak B-patches (two A-patches in the poles and n B-patches along the equator). When two A-patches form sufficiently strong bonds, compared to AB patches (BB patches do not interact), the equilibrium liquid-vapor binodal was found to be re-entrant both in continuum [54,55] and lattice models in two and three dimensions [56–58]. Here, we consider 2A2B colloids where the AA, AB, and BB binding probabilities are dissimilar, and BB patches do interact. By contrast to what was observed experimentally for spherical colloids (without patches) [16], Poisson-like growth is never observed. Depending on the relation between binding probabilities the interface is either in the KPZ or KPZQ universality class with a crossover between the two.

In this work we bring together the fields of interfacial growth and functionalized colloids to address the effect of patch-like anisotropy with short-ranged interactions on the nonequilibrium scaling of a growing interface.

Model. — In an evaporating drop, colloids are dragged to its edge (see fig. 1), and thus we consider advective transport of colloids towards the substrate. Numerically, we consider a bidimensional system where the contact between the edge of the drop and the substrate is a straight line. Similar to the transport mechanism used in ref. [16], colloids are released far away from the substrate at a random lateral position and a vertical straight trajectory towards the substrate is considered. Colloids irreversibly adsorb at the substrate or bind to other colloids. The interaction with the substrate is isotropic and colloids bind to it with a random orientation.

To describe the colloid/colloid interaction we use the model introduced in ref. [45], where an interaction range is defined as a region around the patch parameterized by an angle \(\theta = \pi/6\) with the center of the patch (see the magnified colloid in fig. 1). In the event of a collision with another colloid, the binding occurs only if both interaction ranges overlap. For a successful binding, the probability is checked taking into account the binding probability between the specific patches, and, if binding occurs, the newly aggregated colloid reorients itself so that both patches are aligned. We consider selective interaction between patches, described by distinct binding probabilities.

We assume a chemical bonding between the patches, i.e. highly directional and irreversible within the timescale of interest [59]. We also assume that the process of establishing a chemical bond is thermally activated and characterized by an activation barrier \(E_a\). In general, this barrier is different for AA, AB, and BB bonds. For simplicity, we assume that the higher activation barrier for BB is the same as for AB bonds. The rate of the binding process \(i = \{AA, AB, BB\}\) is Arrhenius-like,

\[
P_i \propto e^{-E_a/k_BT},
\]

where \(k_B\) is the Boltzmann constant and \(T\) is the thermostat temperature. We assume that the prefactor depends only on the frequency of patch-patch collisions and is independent of the patch types. The binding probability of AA, AB, and BB bonds upon colliding is then \(P_{AA}\), \(P_{AB}\), and \(P_{BB}\), respectively. Without loss of generality we consider \(P_{AA} = 1\) and for simplicity \(P_{AB} = P_{BB}\), and define the sticking coefficient \(r_{AB} = P_{AB}/P_{AA}\). AA bonds are favored for low \(r_{AB}\) that promotes the growth of chains.

Results. — We performed simulations for substrates of linear sizes ranging from \(L = 32\) to \(L = 4096\) in units of the colloid diameter \(\sigma\) and adsorption and binding of as many as 8192L colloids.

To study the nonequilibrium scaling of the growing interface we need to compute its morphology. To characterize this morphology we calculate the interfacial roughness \(w\). We divide the system in \(N\) vertical columns of width \(\sigma\), where \(N = L/\sigma\). For each column \(i\) we simulate a downward trajectory of a colloid released from above the maximum height of the film and calculate the height \(h_i\) where it collides with either one colloid or the substrate. The roughness at time \(t\) is then defined as

\[
w(t) = \sqrt{\left\langle h_i(t) - \langle h(t) \rangle \right\rangle^2},
\]

where \(\langle h(t) \rangle = \sum h_i/N\) is averaged over the \(N\) columns. Here, the time \(t\) is defined as the number of absorbed
layers of colloids (equivalent to the experimentally used average height). After the saturation time $t_{\text{sat}}$, the correlation length perpendicular to the growth direction is of the order of the system size and the roughness saturates at $w = w_{\text{sat}}$ [20,60]. Both the saturation roughness and the saturation time scale with the system size as $w_{\text{sat}} \sim L^\alpha$ and $t_{\text{sat}} \sim L^2$, where $\alpha$ is the roughness exponent and $z$ is the dynamical exponent. The short-time behavior of the interface roughness is also a power law given by $w(t) \sim t^\beta$ where $\beta$ is the growth exponent. The interface can then be described by the Family-Vicsek [61] scaling relation,

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

where $f(n)$ is a scaling function. By using the scaling relation and the exponents for different universality classes we can identify the universality class of the growing interface.

In fig. 2 the data collapse of the rescaled roughness is shown, for two limiting values of the sticking coefficient $r_{\text{AB}} = \{0.01, 1\}$. For systems with $r_{\text{AB}} = 1$, fig. 2(a), the data collapse is obtained using the critical exponents of the KPZ universality class, namely $\beta = 1/3$, $\alpha = 1/2$, and $z = 3/2$. However, for $r_{\text{AB}} = 0.01$, fig. 2(b), the data collapse is only observed for the critical exponents of the KPZQ universality class $\beta = 0.63$, $\alpha = 0.63$, and $z = 1.01$. For other values of $r_{\text{AB}}$ we have found that the colloidal network interface is either in the KPZ or KPZQ universality class, for large and small sticking coefficients, respectively.

For $P_{\text{AA}} > P_{\text{AB}} = P_{\text{BB}}$, due to the presence of two strong bonding sites, growth is promoted along the poles, favoring the aggregation of AA chains. These chains are not necessarily aligned vertically and may extend over long lateral regions, blocking the access of new colloids to the underlying colloids. These regions will only have B-patches available for binding, and thus the probability of binding (growth) there is lower. This is expected to have an effect similar to that of quenched noise in eq. (2).

This type of quenched noise also affects the film structure, as shown in fig. 3(a), for the ratio between weak bonds AB/BB and strong bonds AA, $n_c = (N_{\text{AB}} + N_{\text{BB}})/N_{\text{AA}}$ as a function of the distance $z_s$ to the substrate. We note that for $r_{\text{AB}} = 0.01$ the effect of the substrate is observed for the entire range of $z_s$, as evident from the decrease of $n_c$ with $z_s$. By contrast, in systems with $r_{\text{AB}} = 1$, $n_c$ saturates at a nonzero value. For systems with low $r_{\text{AB}}$ and interfacial roughening in the KPZQ class, in fig. 3(b), we found that the “liquid film” never saturates. Rather, we observe a power-law scaling of $n_c(z_s) - n_c(\infty)$ as a function of $z_s$, where $n_c(\infty)$ is the ratio of bonds in the limit of infinite thickness, and $n_c(\infty) = 0.05 \pm 0.01$ for systems with $r_{\text{AB}} = 0.01$. To calculate $n_c(\infty)$, a polynomial fit of $\ln(n_c(z_s) - n_c(\infty))$ as a function of $\ln(z_s)$ of the form $a(\ln(z_s))^3 + b(\ln(z_s)) + c$ was used. A linear dependence is recovered when $a = 0$, giving $n_c(\infty) = 0.05 \pm 0.01$, for $r_{\text{AB}} = 0.01$ (see fig. 3(c)).

Next we investigate how the behavior of the interfacial growth crosses from KPZ to KPZQ by considering different values of the sticking coefficient $r_{\text{AB}}$. For low sticking coefficients, mainly AA bonds are formed and the growth is dominated by chains. Increasing the sticking coefficient, the number of junctions increases, the effect of lateral growth becomes dominant, and the KPZ universality class is recovered.

Figure 4 shows the saturation roughness $w_{\text{sat}}$ rescaled by $L^\alpha$ as a function of the sticking coefficient $r_{\text{AB}}$. In fig. 4(a), the rescaling is done using the roughness exponent of the KPZQ universality class, $\alpha = 0.63$. It is clear that at low values of $r_{\text{AB}}$ the curves collapse indicating that the systems belong to this universality class. Note in fig. 2(b) that the data collapse is observed over two orders of magnitude in size making the possibility of
a finite-size crossover very unlikely. A power-law dependence of the saturation roughness on the sticking coefficient, \( w_{\text{sat}} \sim r_{AB}^{-\lambda} \) is observed, in the KPZQ region, with an exponent \( \lambda = 0.45 \pm 0.01 \). This decrease is related to an increase of the number of junctions which promotes lateral growth and consequently hampers roughening. For systems with \( r_{AB} > 0.1 \) no data collapse is observed with the KPZQ exponents.

Figure 4(b) reveals that using the roughness exponent of KPZ, \( \alpha = 1/2 \), data collapse is observed for \( r_{AB} > 0.5 \), indicating that above that threshold the interface falls into the KPZ universality class. By contrast with the KPZQ systems, the saturation roughness \( w_{\text{sat}} \) does not depend significantly on the sticking coefficient \( r_{AB} \).

The fact that KPZQ is observed over an extended region of \( r_{AB} \) is remarkable since, for previous models of interfacial growth, KPZQ is only found at a critical value of the control parameter (e.g., the force \( F \) in eq. (2)). The reason why the interface is critical for different values of \( r_{AB} \) is likely related to two competing mechanisms that counterbalance to keep the system at criticality. The lower the value of \( r_{AB} \) the lower the probability of binding to a B-patch. However, this also promotes the growth of long AA-chains and these long chains have more available B-patches, compensating the decrease in the binding probability. Figure 5 shows the dependence on \( r_{AB} \), of the ratio of weak to strong bonds in the limit of infinite thickness, \( n_c(\infty) \). The black solid line is the mean-field dependence, given by, \( n_c(\infty) = 3r_{AB} \), where we used the fact that \( P_{AB} = P_{BB} \). We have found that the ratio of bonds is always above the mean-field limit supporting the idea that longer AA chains promote the bonding of B sites, beyond what is expected in the absence of correlations. It is also noteworthy that the typical size of the chains is much smaller than the system size. For example, for systems with \( r_{AB} = 0.01 \) the mean-field value of \( n_c(\infty) = 0.03 \) implies that the average size of the AA chains is of the order of thirty colloids.
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**Conclusions.** – We present a model where we control the assembly of chains or junctions by means of the selective interaction between A and B patches. For similar interactions ($r_{AB} \approx 1$), there is no preferential bonding and junctions are likely to form. For low $r_{AB}$ ($r_{AB} \ll 1$), AA bonds are favored and the growth is dominated by chains. For $r_{AB} = 0$ only chains grow and no interface is formed. One can see the latter limit as a pinned phase with the depinned phase corresponding to the region of KPZ, with a critical depinning transition for the entire region of KPZQ.

The prototypical example of interfacial growth and depinning transitions is the imbibition of a fluid through a randomly disordered porous medium [12,24,27,62,63]. Typically, a fluid invades the pores sequentially as far as the force (fluid pressure) is above the threshold for each pore. While below the critical force invasion is suppressed at a finite distance to the entrance, above it invasion is perpetually sustained and the interface is in the KPZ universality class. Only at the critical force the KPZQ universality class is recovered. This universality class for the interface is then intimately related to a direct percolation transition in the bulk [12]. In our case, the growth occurs due to random addition of colloids to the interface. In order for the interface to grow, colloids need to find their way to the available patches. Since there are two patches on the poles and two along the equator, the growth of individual branches can only be suppressed by steric effects of other branches, but the interface as a whole will always grow [49]. Thus, one does not expect any pinned phase for $r_{AB} > 0$. However, for $r_{AB} \ll 1$ growth is suppressed in regions with a sufficiently large fraction of B-patches and thus KPZQ is obtained. For $r_{AB} = 1$ patches are similar and the interface is in the KPZ universality class. KPZQ is only found at the depinning transition, which in general occurs at a well-defined threshold. Here, we found that the critical depinning regime occurs over a finite range of $r_{AB}$.

Our results have two consequences of practical interest. First, the roughness of the interface can be effectively controlled by the sticking coefficient. Second, our study opens the possibility for an experimental realization of a system with an extended region in the KPZQ universality class, without fine tuning of the control parameters. Possible experimental realizations include the aggregation of colloidal particles functionalized by DNA [36,64] at the edge of a drop [16,17] or in other two-dimensional geometries [65,66].

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