Kinetic roughening of coffee-ring interfaces

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Consider a drop of a liquid with suspended particles which evaporates on a solid substrate. During this process, the suspended solid particles are dragged by capillary flow to the edges of the drop, giving rise to a characteristic ring-like pattern. We have all observed this phenomenon in the coffee blots created at the bottom surface of the cup when there is some coffee left on it; this is why it is called the coffee-ring effect [1]. Formed patterns are complex and may be studied in the context of critical phenomena and universality classes. Here, we have studied the coffee-ring effect as a non-equilibrium growth process.

As shown in [1], the ring-like pattern can be sensitively altered by changes in the morphology of the suspended particles. In particular, when their eccentricity is large enough, the ring disappears. To mimic this effect, we have used a discrete model of patchy colloids [2, 3] with strong and weak bonds, that recreate the anisotropic colloids. The parameter r_{AB} controls the affinity of two distinct patches (A and B), and the morphology of the aggregates depends on this ratio, as shown in Fig. 1. Thus, the model reproduces the different growth behaviours depending on particle shape: large values of r_{AB} corresponds to spherical colloids and decreasing values of r_{AB} to increasing colloids eccentricities.

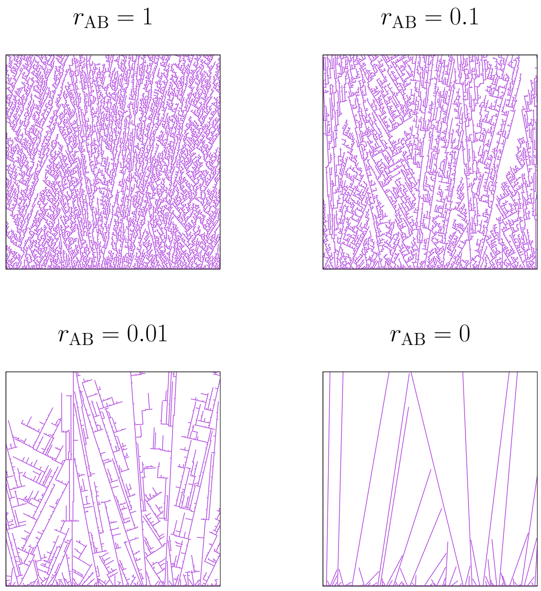

Fig. 1. Morphology of the aggregates calculated for several r_{AB} values (i.e., colloid eccentricities).

We have performed extensive numerical simulations for $r_{\mathrm{AB}} \in [0, 1]$. We appreciate a distinctive behaviour of the system for $r_{\mathrm{AB}} = 0$, when only AA bonds form. This means that secondary branches do not occur; as a result, the front stops when some branches reach the system boundary.

By studying the surface roughness and the correlation length for different values of r_{AB}, we have computed the critical exponents characterising front fluctuations for coffee-ring aggregates. Our results (see Table 1) seem compatible with the quenched Kardar-Parisi-Zhang (QKPZ) universality class exponents $\beta = 0.63$, $z = 1.01$ and $\alpha = 0.63$.

r_{AB}	β	z	α
1	0.55(2)	1.06(6)	0.64(4)
0.1	0.64(2)	1.05(11)	0.69(6)
0.01	0.691(14)	1.00(4)	0.89(4)
0.001	0.690(14)	1.13(12)	0.72(7)
0.0001	0.609(10)	1.0(3)	0.74(18)

Table 1. Critical exponents the evaporating drop. Into brackets, the errors estimated by the jackknife procedure.

The height-difference correlation function $C_2(r, t)$ shows anomalous scaling behavior. The collapse of the correlation function using the QKPZ exponents (Fig. 2) fits to $x^{-2\alpha'}$ for $x \ll 1$, with $x = r/t^{1/z}$ and $\alpha' = \alpha - \alpha_{\mathrm{loc}} \neq 0$. This allows us to measure the α_{loc} exponent. The nature of the anomalous scaling may be clarified by the structure factors $S(q, t)$ analysis. This shows a systematic shift upwards with time and scales with the wave vector as $S(q, t) \sim q^{-(2\alpha_{\mathrm{loc}}+1)}$, which evidences intrinsic anomalous scaling.

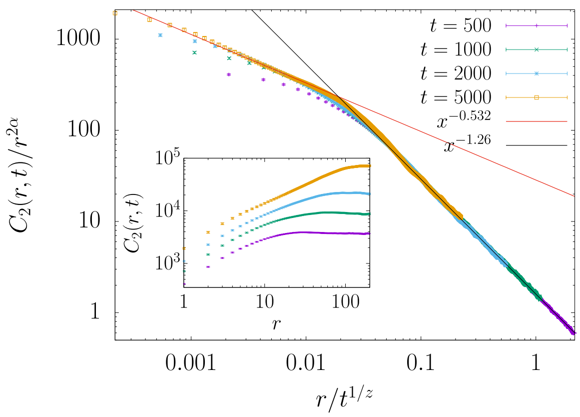

Fig. 2. Collapse of $C_2(r, t)$ for $r_{\mathrm{AB}} = 0.001$ at different times. Solid lines are the fits for $x \leq 0.01$ and $x \geq 0.1$ at $t = 5000$. Inset: $C_2(r, t)$ vs. r plot.

[1] P. J. Yunker, T. Still, M. A. Lohr, and A. G. Yodh, Nature **476**, 308 (2011).

[2] C. S. Dias, N. A. Araújo, and M. M. Telo Da Gama, Eur. Phys. Lett. **107**, 56002 (2014).

[3] C. S. Dias, P. J. Yunker, A. G. Yodh, N. A. Araújo, and M. M. Telo Da Gama, Soft Matter **14**, 1903 (2018).