Supplementary Material for: Nucleated dewetting in supported ultra-thin liquid films with hydrodynamic slip

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(Dated: June 7, 2017)

EFFECTIVE INTERFACE POTENTIAL AND SPINODAL WAVELENGTH

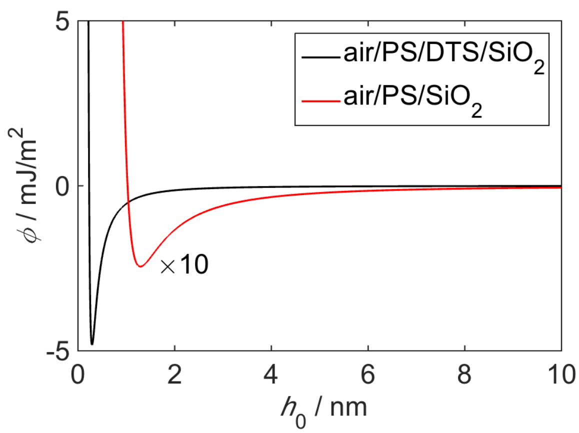

FIG. S1. Effective interface potentials, ϕ, for PS on a DTS coated SiO_2 wafer and for PS on a SiO_2 wafer. For clarity ϕ for the latter has been multiplied by ten. We have made use of $C_{\mathrm{DTS}} = 8.2 \times 10^{-26}\,\mathrm{J/nm^6}$, $C_{\mathrm{SiO_2}} = 6.3 \times 10^{-22}\,\mathrm{J/nm^6}$, and $A = 2.05 \times 10^{-20}$ J, as well as Eq. 1 of the main text.

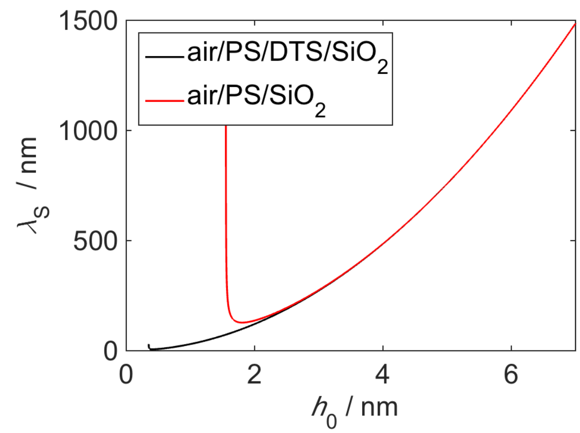

FIG. S2. Spinodal wavelengths predicted using $\lambda_{\mathrm{S}} = \sqrt{-8\pi^2\sigma/\phi''}$ and the effective interface potentials of Fig. S1 and $\sigma = 0.038\,\mathrm{J/m^2}$. We note that the predicted spinodal wavelengths do not significantly differ for $h_0 > 3$ nm for the two cases considered here.

MINKOWSKI MEASURES; POWER SPECTRAL DENSITIES

Different methods are suitable to analyze correlations in point patterns, in our case, Minkowski measures have shown to be extremely convenient, since they are able to find not only two-point correlations (like a Fourier transformation oder a pair correlation function g(r)), but also capture higher-order correlations [1]. In the very same way as in earlier studies, we have analyzed the statistical distribution of the hole sites by Minkowski measures [2, 3]. In two dimensions (like for our point set of hole sites), three Minkowski measures completely describe the distribution and there are analytical descriptions of what to expect for a random (Poissonian) set of sites. This is the clear strength of Minkowski measures, a random process can unambiguously be detected analytically. Deviations of that expectation then show that the hole sites are correlated.

One Minkowski measure is the Euler characteristic, χ, which quantifies the connectivity of a distribution of objects – in this case the distribution and connectivity of the holes seen in Fig. 1. χ is computed by placing disks of radius r at the center of every hole (see Fig. S3a)), and is thereby only a function of the number of holes and the disk radius, $\chi = \chi(r, N)$. It is also possible to analytically calculate χ for a Poisson distribution of holes, as described in Refs. [4–6]. Fig. S3b) depicts the Euler characteristic of the experiments shown on Fig. 1 and that obtained by the theory for a Poisson distribution (eq. 24 in [5]):

$$\chi(r) = \pi\rho(1 - \pi r^2\rho)e^{-\pi r^2\rho}\ , \tag{S1}$$

where ρ is the number density of disks, easily accessed from the experimental data. The prediction of the Poisson distribution, a universial curve in the normalized representation of Fig. S3b), is not followed by the hole formation of spinodally dewetting films, as seen in [3, 7] and confirmed here for the liquid films on the bare SiO_2 substrate; the power spectral densities of Fig. S4 show furthermore a well defined peak at the expected spinodal wavelength, giving

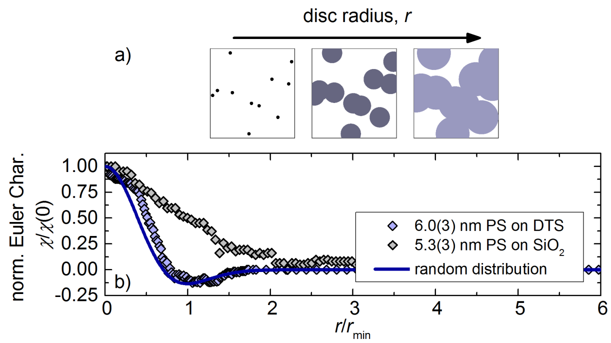

FIG. S3. a) Schematic depiction of the procedure for determining the Euler characteristic, χ: hole centers are identified, and disks of variable radius r are placed at each center. As the radius of each circle grows, fewer and fewer independent objects cover the plane, thus reducing χ. b) Statistical distribution of holes revealed by the normalized χ, for films at a similar dewetted area (symbols), and the theoretical prediction for uncorrelated holes (line) with no fitting parameter.

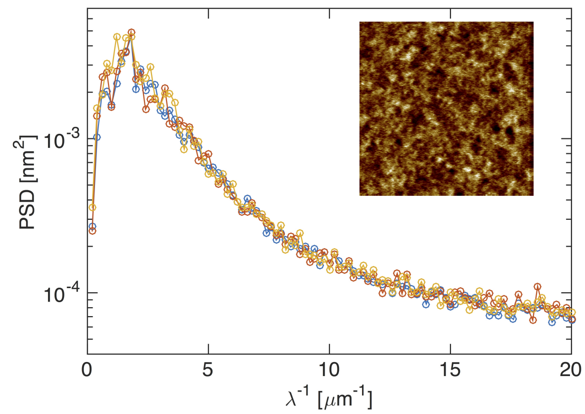

FIG. S4. Power spectral densities (PSD) of three sequential *in situ* AFM images (inset, horizontal scan size $5 \times 5\,\mu\mathrm{m}^2$, vertical scale 1.8 nm), for a 6 nm PS film dewetting from SiO_2, taken at 115 °C with $36\,\mathrm{min} \leq t \leq 43\,\mathrm{min}$. The positions of the maxima of the three curves coincide and correspond very well with the expected spinodal wavelength predicted using the effective interface potential shown in Fig. S1.

further evidence for the spinodal mechanism governing the film breakup on SiO_2 substrates. In contrast, the Euler characteristic for dewetting films on DTS is well captured by the uncorrelated random distribution, which proves that the dewetting process on DTS cannot originate from a spinodal process.

FREE ENERGY COMPONENTS

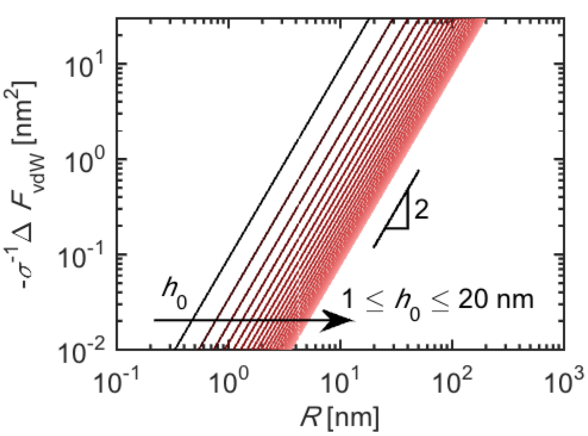

FIG. S5. Representation of the van der Waals contribution to the free energy, ΔF_{vdw} as computed from Eqs. (1) and (4). The slope of the curves in this log-log representation confirms the relation $\Delta F_{\mathrm{vdW}} = -c_{\mathrm{vdW}} R^2$. *n.b.* the minus sign on the vertical axis allowing for a log representation. The arrow points in the direction of increasing h_0.

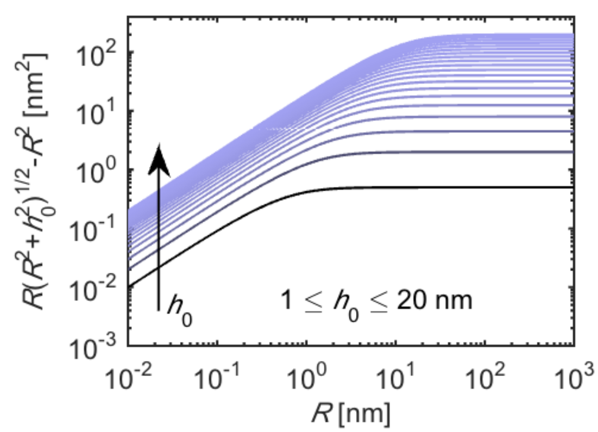

FIG. S6. Representation of the capillary contribution to the free energy, $\Delta F_{\mathrm{surf}}/(\pi\sigma)$ in Eqs. (2) and (3). The arrow points in the direction of increasing h_0.

HOLE DENSITY ON AF 1600

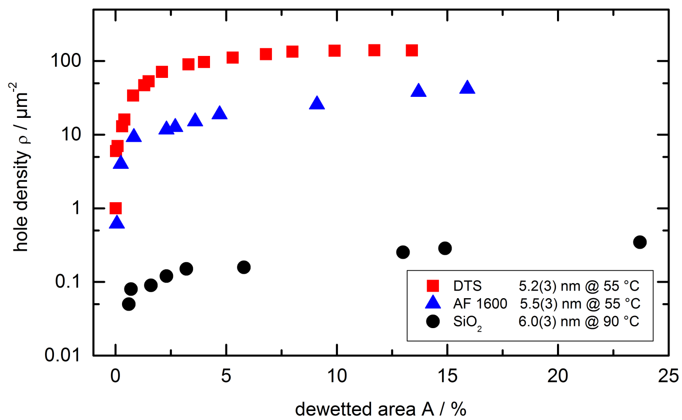

FIG. S7. Hole densities for ultra thin PS films dewetting from three different substrates nominally susceptible to spinodal dewetting, but which is shown only for SiO_2 as described in the main text. We show the hole density as a function of the dewetted area for SiO_2, AF 1600-coated SiO_2 wafers, and DTS-coated SiO_2 wafers. Significant enhancements of the hole density are observed for DTS and AF 1600 as compared to SiO_2.

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[1] K. Mecke, International Journal of Modern Physics B **9**, 861 (1998).
[2] K. Jacobs, S. Herminghaus, and K. R. Mecke, Langmuir **14**, 965 (1998).
[3] S. Herminghaus, K. Jacobs, G. Schatz, K. Mecke, J. Bischof, A. Fery, M. Ibn-Elhaj, and S. Schlagowski, Science **282**, 916 (1998).
[4] S. Chiu, D. Stoyan, W. S. Kendall, and J. Mecke, *Stochastic geometry and its applications*, Vol. 3 (Wiley, 1996).
[5] C. Arns, M. Knackstedt, and K. Mecke, Colloids and Surfaces A **241**, 351 (2004).
[6] K. Mecke and D. Stoyan, Biometrical Journal **47**, 1 (2005).
[7] J. Becker, G. Grün, R. Seemann, H. Mantz, K. Jacobs, K. Mecke, and R. Blossey, Nat. Mat. **2**, 59 (2003).