

# Thin Liquid Polymer Films Rupture via Defects

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The standard rupture scenario of thin polymer films on solid substrates is investigated in detail. The geometry of the dewetting structure is analyzed by means of the Minkowski functionals in two dimensions. Furthermore, the temporal behavior and the impact of ambient conditions are considered. In contrast to what has been frequently asserted, we show that spinodal dewetting does very probably not play any significant role in the rupture process. On the contrary, it is demonstrated that rupture is dominated by nucleation from defects, which are intrinsic to the polymer due to its peculiar morphology. It is concluded that polymer films on solid surfaces are either stable (in the case of complete wetting) or unstable, but never metastable.

## Introduction

Thin polymer films play a substantial role in modern technology: polymeric coatings preserve, isolate, or just decorate the underlying material and they help to achieve high-resolution TV screens and color films, just to mention a few applications. The question of film stability is one of the basic questions to be answered. Color films should work in a large range of temperatures; coatings should cover the substrate completely and be stable for years. Therefore, a vast amount of research has been dedicated to the problem of stability of polymer films on solid substrates.<sup>1</sup> However, a large number of questions have yet remained open, especially concerning the early stage of film rupture, which occurs if the film does not wet the substrate. In many experiments involving different polymers and substrates, rupture has been observed to proceed via the formation of circular holes whose radius grows in time, finally leading to dewetting of the whole film.<sup>2–8</sup> However, the mechanism of initial hole formation, which determines the film stability, is still under debate.

Two candidate mechanisms are discussed which may initiate rupture: (i) nucleation, e.g., from defects or impurities in the film, and (ii) spontaneous film rupture, if long-range interactions (such as the van der Waals (vdW) force) between the liquid film material and the substrate disfavor wetting. In the latter case, thermal fluctuations in film thickness experience a driving force and grow exponentially with time, leading to dewetting as soon as the amplitude reaches the size of the film thickness. For this mechanism the term “spinodal dewetting” has been coined in analogy to the symmetry breaking mechanism

involved in decomposition processes.<sup>9,10</sup> In this kind of dynamical instabilities, there usually exists a critical wavelength the corresponding amplitude of which grows the fastest, and thus determines the dominant wavelength,  $\lambda_c$ . If the long-range forces are due to the (nonretarded) vdW interaction,  $\lambda_c$  should scale theoretically<sup>11,12</sup> as the square of the film thickness,  $\lambda_c \propto h^2$ . In this case, one thus expects a dewetting structure with a characteristic length scale behaving correspondingly. If one assumes that every valley in the initial surface ripple (or at least a significant fraction of valleys) leads eventually to the formation of a hole, the density of holes is thus expected to scale as the inverse fourth power of the film thickness.

Experimentally it was observed<sup>3,4,13,14</sup> that the number density,  $\rho$ , of holes appearing during the rupture process scaled indeed according to the predicted scaling law  $\rho \propto h^{-4}$ . This was repeatedly taken as evidence of a spinodal dewetting process. In the present paper we show that, in contrast to what is widely believed, nucleation by defects is the dominating mechanism leading to rupture of polymer films. Moreover, we give some evidence about the type of defects involved, strongly suggesting that metastable polymer films on solid surfaces do not exist at atmospheric pressure.

## Experimental Section

As a convenient model system we chose polystyrene (PS) films on silicon wafers, which has been used frequently as a standard system, in particular for investigations of the rupture mechanism. The polymer films were prepared by spin casting from a toluene solution of polystyrene (PS) ( $M_w$  from 65 to 600 kg/mol,  $M_w/M_n = 1.02$ ,  $T_g = 100^\circ\text{C}$ ; Polymer Standards Service, Mainz, Germany) onto freshly cleaved mica sheets (indian ruby Muscovite mica, Mica New York Corporation, New York, USA). From there they were floated onto a clean, deionized water surface and picked up

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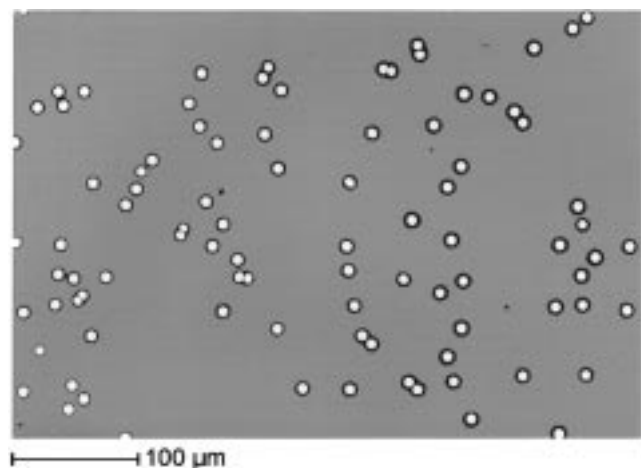
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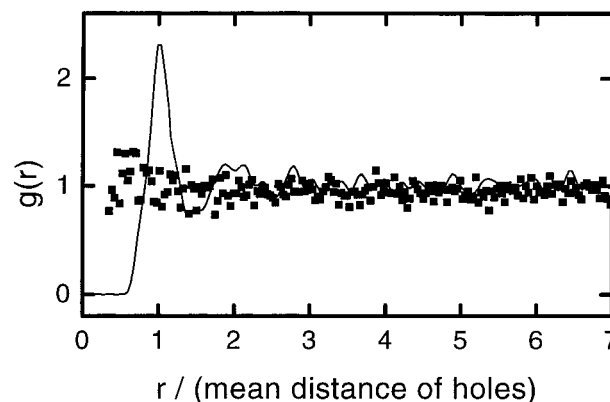
**Figure 1.** Typical rupture scenario in a polymer film. A 47 nm thick film of polystyrene on a silanized silicon wafer is shown after annealing for 7 min to 130 °C. Circular holes appear with a very narrow size distribution. Their radius grows with time.

with silanized<sup>15</sup> Si wafers. For the silanization with octadecyltrichlorosilane (OTS, Aldrich Chemie, Steinheim, Germany) we followed standard procedures,<sup>16,17</sup> consistently reaching contact angles of 112(1)° for a sessile drop of Millipore water. The roughness of the OTS layers and of the polystyrene films, as determined by atomic force microscopy (AFM) was below 1 nm. Preparation and most of the characterization took place in a class 100 clean room atmosphere. Annealing took place *in situ* under the microscope. Temperatures varying from 114 to 133 °C could be held constant at an accuracy of 0.2 °C; the final annealing temperature was achieved within less than 2 s after the sample had been put onto the oven, as checked by melting experiments with indium grains ( $T_M = 150$  °C) on top of samples. Scanning electron microscopy (SEM) and AFM scans at room temperature gave insight in the topography of films and holes.

## Results and Discussion

Figure 1 shows the typical rupture scenario of a thin polystyrene film on a nonwettable substrate. A 47(2) nm thick PS film ( $M_w = 600$  kg/mol) is shown, annealed for 7.0 min at 130 °C. The average diameter of the holes, whose shape was found invariably to be circular,<sup>18</sup> is 8.4 μm; the width of the distribution is 0.2 μm. This narrow size distribution reflects the fact that almost all of the holes form within a very sharp time window. The areal density of holes,  $\rho$ , was found to scale roughly as  $\rho \propto h^{-4}$ , in accordance with the above-mentioned results obtained by other authors, as discussed above. Similarly, the (apparently) random spatial distribution of holes is qualitatively identical to what has been generally observed before. It is this spatial distribution onto which we will concentrate next.

If hydrodynamically unstable surface ripples were responsible for the formation of the holes (spinodal dewetting), correlations were to be expected in the geometry of the hole arrangement reflecting the presence of a critical wavelength,  $\lambda_c$ . In contrast, a purely Poissonian distribution of hole positions would be clear counterevidence of a spinodal process. In a first step, we calculated the two-point correlation function of the point



**Figure 2.** Two-point correlation function,  $g(r)$ , for the hole positions in a dewetting polymer film (full circles) and for the valley positions of undulations in a liquid gold film dewetting via unstable surface waves (solid line).  $r$  is given in units of the mean distance of objects.

set represented by the hole positions. This is displayed in Figure 2 by the full circles. No feature indicative of a dominant wavelength can be seen. Direct conclusions about the nature of the underlying process should not be drawn from the two-point correlation function alone. However, the latter is known to be quite ineffective in detecting higher order correlations, and completely different spatial patterns may yield very similar results. In particular, the impact of the strong nonlinearity of the van der Waals potential on the dynamics of surface undulations, and thus on the details of the emerging dewetting structure, has only been studied in quite crude (i.e., one-dimensional) models.<sup>13,19,20</sup>

We therefore used the concept of Minkowski functionals to obtain a valuable characterization of the point set representing the positions of the holes in the film. Minkowski functionals are known to yield stable results with small statistical errors even for small samples, which is of particular importance for the analysis of experimental data. They provide statistically unbiased descriptors which contain features of  $n$ -point correlation functions at any order  $n$  and are efficient in discriminating theoretical models.<sup>21–23</sup> We introduce a “coverage” of the point set by assigning to each member of the set the center of a disk, each with the same radius,  $r$ . The coverage is now defined as the set union of all disks. The scale-dependent morphological features of this coverage are then explored by varying the radius of the disk and calculating the Minkowski measures of the coverage as a function of  $r$ . In two dimensions, the Minkowski functionals are the covered area  $F$ , the boundary length  $U$ , and the Euler characteristic  $\chi$  of the coverage. The latter is defined as the integral over the boundary curvature, extended along the entire boundary. We used for the analysis the normalized length  $x := r/L$  ( $L$  denoting the average hole distance) and the transformed functions

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(18) The shape of the holes deviates from a circle by less than 2% (difference between small and large half axis).

$$F^*(x) := \frac{1}{\pi r^2 N} \ln \left( 1 - \frac{F(x)}{\Omega} \right)$$

$$U^*(x) := \frac{U(x)}{2\pi r N (1 - F(x)/\Omega)}$$

and

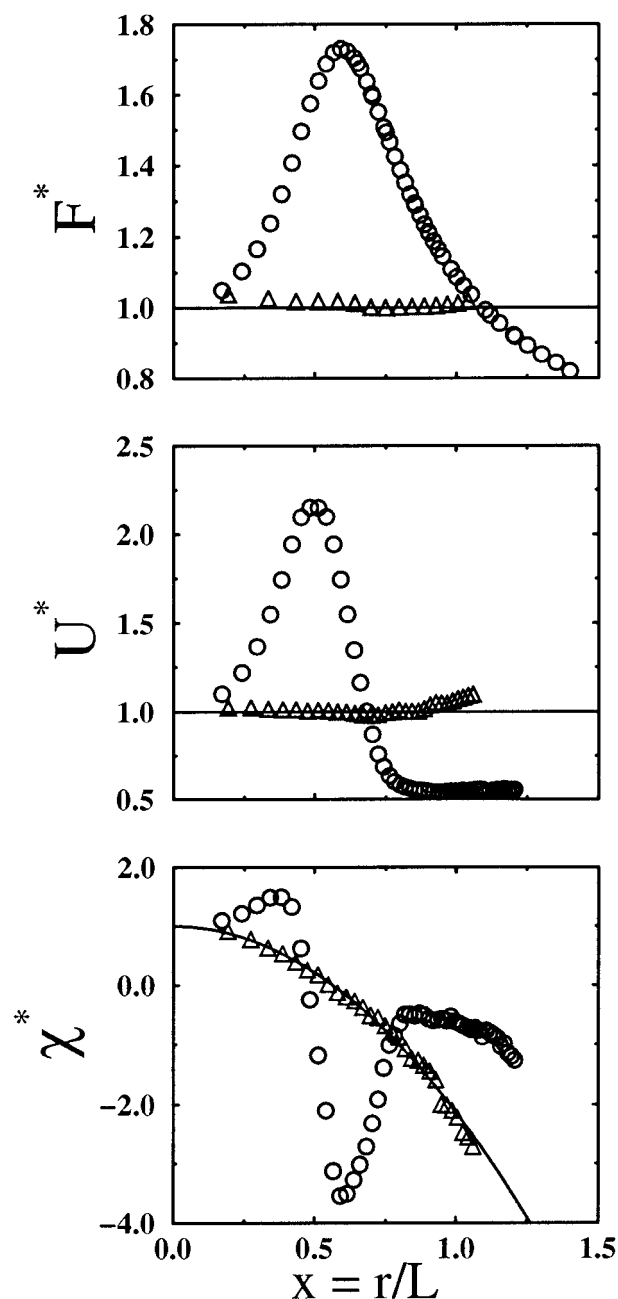
$$\chi^* := \frac{\chi(x)}{N(1 - F(x)/\Omega)}$$

$\Omega$  denotes the total area of the sample. In this form,  $F^* = 1$ ,  $U^* = 1$ , and  $\chi^* = 1 - \pi x^2$  are the expectations for randomly (Poisson) distributed points.

In Figure 3, the behavior of the three Minkowski measures is shown as triangles for the point set given by the centers of the holes, a section of which is displayed in Figure 1.  $F^*$ ,  $U^*$ , and  $\chi^*$ , the expected measures for a Poissonian point set, are represented as solid lines. Excellent agreement is found for all three functionals, the small deviations for larger radii being solely due to finite size effects which occur when  $r$  comes within the range of the system size. This demonstrates clearly that there are no lateral correlations present (neither first order nor higher order) in the distribution of the holes in the polymer film. We employed the same analysis also to published data of hole distributions<sup>3,13</sup> and found, again, no significant deviation from a Poissonian distribution.

Let us consider for comparison the spinodal-dewetting pattern of a liquid gold film that has been recently reported.<sup>24</sup> For this system, an unstable surface ripple with a dominant wavelength,  $\lambda_c$ , could be clearly identified. We have analyzed the positions of the valleys of the observed undulations (as published in ref 24), as depicted in Figure 4. Their two-point correlation function, which is displayed as the solid line in Figure 2, shows a pronounced peak at the mean distance of the holes. This already demonstrates the strong deviation from a statistical distribution. Furthermore, the positions of the valleys have been used as a point set to which the same calculation of the Minkowski functionals as above was applied. The results are shown as open circles in Figure 3. The substantial deviation from the Poissonian is evident. It is thus demonstrated that the dewetting structure of the only system reported yet which dewets by hydrodynamically unstable surface waves is indeed, as expected, strongly different from a Poissonian. An involvement of a spinodal process in the rupture of the polymer film, however, is not apparent, as Figure 3 suggests.

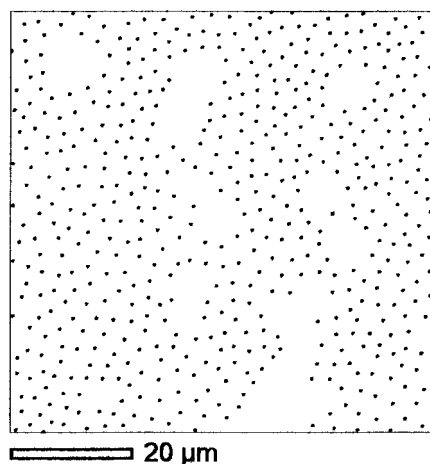
Furthermore, we investigated the temporal behavior of the rupture process. According to theory, the rupture time,  $\tau$ , which denotes the time after which the holes form, should be equal for all holes and scale as  $\tau \propto h^{5,12}$ . In order to obtain the rupture time, the diameters of a number of holes were recorded as a function of time and extrapolated to zero radius. This gave a reasonable estimate of  $\tau$  with a statistical scattering of less than 10%. Figure 5 shows that the rupture times obtained in this way are only weakly dependent on film thickness (a fit yields  $\tau \propto h^{0.6 \pm 0.3}$ ), as opposed to the predicted scaling exponent of 5 (dashed line). Even films with large thicknesses of more than 300 nm, which is beyond the vdW range, break up within some hundred seconds. It is thus demonstrated that there is neither a lateral correlation in the hole distribution nor a temporal behavior even close to what is predicted for spinodal dewetting. This rules out a spinodal dewetting process to be responsible for the hole formation.



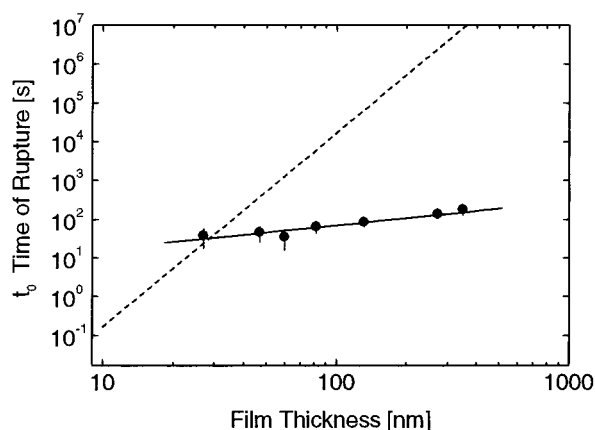
**Figure 3.** Morphological measures  $F^*$ ,  $U^*$ , and  $\chi^*$  as a function of the normalized radius,  $x = r/L$ , of the disks with mean distance  $L$ : solid lines, behavior expected for a purely Poissonian set; triangles, hole positions in polymer film; circles, valley positions of undulations in liquid gold film.

It should be noted here that a thermally activated hole formation process would yield a steep exponential behavior,<sup>25</sup> which is clearly not observed. Furthermore, this process would proceed independently at different places on the sample, and hole formation would necessarily continue to take place as long as the sample has not fully dewetted. This is at variance with observation, since almost all of the holes are present shortly after dewetting starts, as it is clearly seen in Figure 6. We have thus ruled out any dynamical instability as well as thermally activated hole formation as the processes responsible for the generic polymer film rupture scenario. The only remaining possibility is heterogeneous nucleation from defects in the film or at the substrate surface. It should

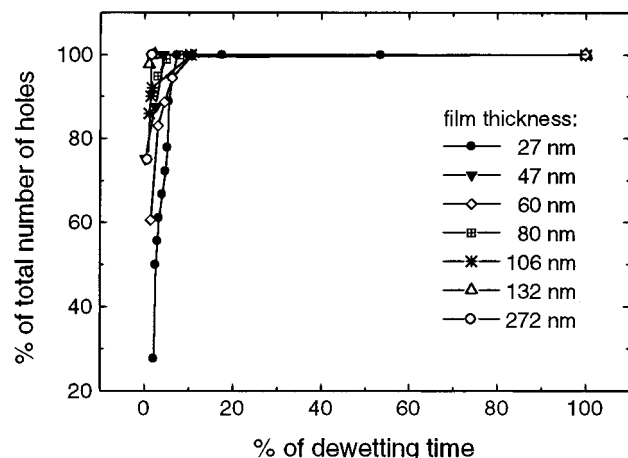
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**Figure 4.** Positions of the valleys of the thickness undulations found in a gold film dewetting via unstable surface waves (as published in ref 24). The existence of a preferential next-neighbor distance is obvious.



**Figure 5.** The rupture time,  $\tau$ , as determined by extrapolating the hole diameters to zero vs the film thickness,  $h$ . The dashed line is the theoretical prediction for spinodal dewetting.



**Figure 6.** Number of holes present on the sample, as a function of time. After the characteristic rupture time, no further breakup is observed until the whole film has dewetted.

be mentioned that rupture took place although the preparation conditions<sup>26</sup> had been improved such that neither by optical microscopy nor by SEM or AFM, particles (dust, etc.) which might have been candidate nuclei could be detected in the centers of the holes (particles larger than 8 nm would have been detected safely). However, we did not yet consider candidate defects that

may be intrinsic to the polymer film itself, due to its intrinsically disordered morphology. In fact, it is well-known that at atmospheric pressure polymers take up certain amounts of gas and that the gas does not distribute uniformly but accumulates in certain places, where the material is less dense.<sup>27</sup> It may thus be justly spoken of a porous material, and the usually applied continuum model may be too simplistic.

In order to investigate whether defects of this type are involved in the rupture process, we repeated our studies at different ambient pressures. Experiments were carried out in air, nitrogen, argon, and helium atmospheres. A number of identically prepared samples were sealed in glass ampules, which were evacuated before sealing to a desired pressure between atmospheric pressure and  $10^{-5}$  Pa. Afterward, the ampules were heated to 130 °C. In a second series of experiments, samples were placed directly into a vacuum oven, the pressure of which could be varied in a wide range, and annealed up to a maximum temperature of 200 °C. It was generally found that when the experiments were performed under vacuum below a pressure of about 1 mbar, rupture could be *completely suppressed*, provided the substrate had been properly cleaned. Irrespective of the gas used, a pressure of 10 mbar or more safely induced the formation of holes, while a pressure of 1 mbar or less reliably suppressed any rupture. This demonstrates that the properties of the defects from which the holes nucleate are strongly dependent on the external gas pressure as one would expect from the above-mentioned gas-filled pores present at ambient pressure. It is clear that the vdW interaction of these pores is different from that of the surrounding bulk polymer and that they may thus serve as nucleation sites. This would also explain why spinodal dewetting is quite easily observed in liquid metal films but seems to have never been seen in polymer films, since metal films are more compact and lack the sensitivity to atmospheric conditions, which has been reported for polymers.<sup>4,27</sup> With defects present, dewetting by nucleation is always completed before a spinodal wave has a chance to build up.

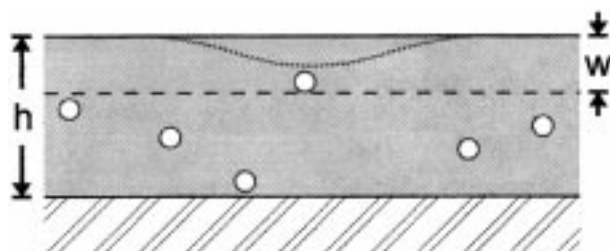
The remaining task is to explain the dependence of the hole density upon the film thickness,  $h$ , on the basis of the model of a porous polymer film (cf. Figure 7). A pore, or a cluster of pores, is a region of reduced density and thus of reduced refractive index. The film material between such a region and the film surface thus tends to drain away laterally by virtue of the van der Waals force,<sup>28</sup> provided the distance of the pore to the film surface does not exceed a few nanometers, as indicated by the dashed line in Figure 7. This gives rise to an indentation of the film above the pore (dotted line) which finally reaches the pore, resulting in their rupture and disappearance. Afterward, the indentation relaxes by means of the surface tension of the film material, restoring a smooth film surface.

If, however, there is a second pore below the indentation, the latter will continue to grow until also this second pore is healed, and so on. The probability of an indentation to grow to a certain depth is thus equal to the probability of

(26) A crucial source of defects was found to be the toluene, even at spectroscopical grade. Only with ultrapure toluene (Selectipur Toluol, Merck, Darmstadt, Germany) could we achieve satisfactory results. Moreover, the Si substrate was cleaned before silanization with the help of a "Snowjet" (Applied Surface Technologies, New Providence, NJ), a high-velocity CO<sub>2</sub> gas jet, consisting of a mixture of crystals and gas. Thereby, dust particles remaining from cutting the wafer were safely removed.

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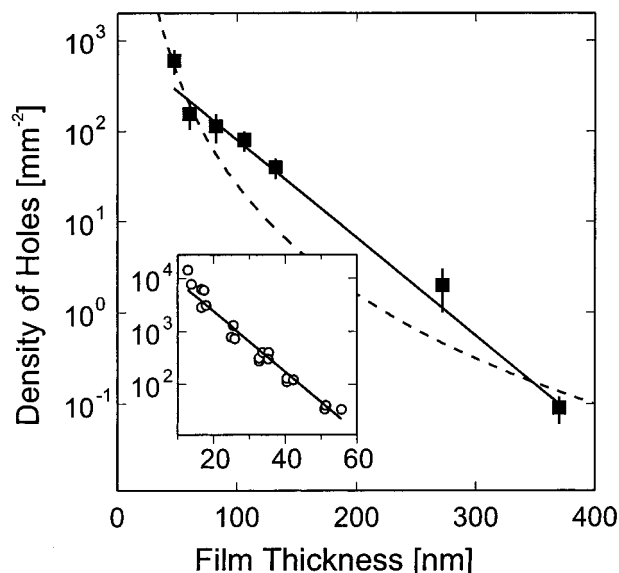
**Figure 7.** Model of a porous polymer film in surrounding gas. The dashed line indicates the effective range,  $w$ , of the van der Waals interaction; the dotted line sketches the indentation growing above a pore close to the surface.

finding an appropriate "consecutive" ensemble of pores beneath its position of first formation, all within an area determined by the width of the indentation. Irrespective of details, this probability scales thus exponentially with the indentation depth to be reached. The density of holes nucleated by indentations having reached the substrate surface is then expected to scale exponentially with the film thickness. In Figure 8, we plotted our data as well as published data (inset) along with an exponential fit. It is clearly seen that in both cases good agreement is obtained. Also shown is a fit of the  $h^{-4}$  scaling law proposed earlier (dashed line), which is obviously less satisfactory for our data. For extracting information on the film material from the experiment, a refinement of our rather crude model, including a study of the dynamical shape of the indentations, will be necessary.

We were delighted to see that indentations like the ones proposed above have been indeed observed recently by scanning force microscopy of polystyrene films on non-wettable silicon wafers.<sup>8</sup> Although they have been interpreted as being due to spinodal dewetting, which we tend to doubt according to the discussion presented in this work, the data provide valuable insight into their dynamics. It was reported that the depth,  $d$ , of the indentations grows faster than linear with time, and we found that their data could be reasonably well fitted by a growth law  $d \propto t^2$ . Accordingly, the rupture time,  $\tau$ , measured in our experiments should scale roughly as  $\tau \propto h^{0.5}$ , which is well consistent with our observation, as Figure 5 shows.

### Summary

In conclusion, we have shown by careful analysis of the standard dewetting scenario of polymer films on solid



**Figure 8.** Density of holes vs the film thickness. Our data are well represented by the exponential (solid line) corresponding to our model. The prediction for spinodal dewetting (dashed line) fits much less satisfactorily. The inset demonstrates that also the data of other authors<sup>3</sup> may be well fitted by an exponential.

surfaces that spinodal dewetting does very probably not play any significant role. On the contrary, it could be demonstrated that rupture is dominated by nucleation from defects. Furthermore, strong evidence was given that these defects are intrinsic to the polymer due to its peculiar morphology, as opposed to other materials (such as metals). Since this means that at atmospheric pressure, there are always nuclei present which mediate rupture and dewetting, we arrive at the conclusion that, provided our model turns out to be correct, polymer films on solid surfaces are either stable (in the case of complete wetting) or unstable, but never metastable.

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