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# Dewetting of a thin polymer film under shear

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## Abstract

The objective of this work is to study the role of shear on the rupture of ultra-thin polymer films. To do so, a finite-difference numerical scheme for the resolution of the thin film equation was set up taking into account capillary and van der Waals (vdW) forces. This method was validated by comparing the dynamics obtained from an initial harmonic perturbation to established theoretical predictions. With the addition of shear, three regimes have then been evidenced as a function of the shear rate. In the case of low shear rates the rupture is delayed when compared to the no-shear problem, while at higher shear rates it is even suppressed: the perturbed interface goes back to its unperturbed state over time. In between these two limiting regimes, a transient one in which shear and vdW forces balance each other, leading to a non-monotonic temporal evolution of the perturbed interface, has been identified. While a linear analysis is sufficient to describe the rupture time in the absence of shear, the nonlinearities appear to be essential otherwise.

*Keywords:* Thin films, Lubrication, Polymers, Dewetting, Shear, Nanolayer coextrusion

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## 1. Introduction

2 Nanolayer coextrusion, an innovative process allowing the combination  
3 of at least two polymers in a stratified film or membrane having a total  
4 thickness on the order of 100  $\mu\text{m}$  but composed of thousands of alternating  
5 nanometric layers, has gained an increased interest in the past few years [1, 2].  
6 This process offers unique opportunities to explore fundamental questions on  
7 the effects of confinement on polymer properties, such as crystallization [3],  
8 chain mobility and structural relaxation [4, 5, 6] or interfacial phenomena

9 [7, 8, 9], as well as to design new nanostructured materials with novel or  
10 enhanced properties (mechanical, optical, conductive, gas barrier properties,  
11 etc.) [10].

12 However, one strong limitation of the process lies in possible layer breakups,  
13 observed by several authors on different polymer pairs when reducing the  
14 layer thickness [11, 12, 13]. In a previous study, we investigated this phe-  
15 nomenon in polystyrene (PS)/poly(methyl methacrylate) (PMMA) nanolay-  
16 ered films [14] and evidenced the existence of a critical thickness around 10  
17 nm, below which the layers rupture spontaneously, independently of the pro-  
18 cessing conditions. We then proposed a mechanism responsible for this layer  
19 breakup, similar to the one leading to the dewetting of an ultra-thin polymer  
20 monolayer deposited on a solid substrate, as firstly observed by Reiter et al.  
21 [15] and subsequently explained by Brochard et al. [16].

22 In nanolayer coextrusion, when the layer thickness is very small - typically  
23 below 100 nm-, attractive long-range forces (*i.e.* van der Waals forces) be-  
24 tween the two adjacent layers cannot be neglected. Below a critical thickness  
25 around 10 nm, they become dominant over the stabilizing capillary forces.  
26 In consequence, they may amplify any interfacial instability such as the one  
27 due to thermal fluctuations, eventually leading to the layer breakup. Sev-  
28 eral model experiments on spin-coated three-layer systems were subsequently  
29 proposed to confirm this scenario [17, 18]. Comparing the characteristic  
30 dewetting times in a model trilayer system to typical residence times in the  
31 nanolayer coextrusion process, we also suggested that the shear induced in  
32 the nanolayer process may delay the layer rupture, *i.e.* may stabilize the  
33 layers against rupture.

34 Similar questions have been addressed for many years in the field of fluid  
35 mechanics, where the stability of ultra-thin liquid films has been a concern in  
36 several industrial applications, such as coating processes [19] or lithographic  
37 printing [20]. The stability of thin films has been the subject of many theo-  
38 retical and experimental studies (see for example the reviews of Oron et  
39 al. [21] and Craster et al. [22]). The pioneering works of Vrij [23] and  
40 Sheludko [24] focused on the mechanism of spontaneous rupture of a thin  
41 liquid film deposited on a solid substrate. Using slightly different approaches  
42 - thermodynamic treatment for Sheludko and diffusion equation for Vrij-,  
43 they showed for the first time that the amplification by vdW forces of small  
44 irregularities at the film's free surface may lead to a decrease of the total free  
45 energy despite the increasing surface, and consequently induce film rupture.  
46 They proposed a critical thickness below which the destabilizing vdW forces

47 become dominant over the capillary forces, a critical wavelength of the initial  
48 irregularities above which the film is unstable, as well as a growth rate of the  
49 perturbation and a characteristic time for rupture.

50 A more systematic and rigorous approach, developed by Ruckenstein and  
51 Jain [25], was based on a linear stability analysis of the Navier-Stokes equa-  
52 tions. They assumed that the amplification of small perturbations at the  
53 film interface generates a flow in the film. Due to its small thickness, the  
54 lubrication approximation was employed. The long-range vdW forces were  
55 accounted for through a disjoining pressure term as proposed by Derjaguin  
56 [26]. Even if this stability analysis is theoretically valid for small perturba-  
57 tions only, information about the conditions leading to film rupture could  
58 be obtained. In particular, Ruckenstein and Jain showed that the critical  
59 wavelength of the initial periodic disturbance leading to rupture was much  
60 larger than the film thickness. These results laid the groundwork for sub-  
61 sequent studies that investigated the nonlinear effects on thin film rupture  
62 using either a perturbative analysis [27] or numerical computations [28]. In  
63 the latter study, the authors derived a highly non-linear partial differential  
64 equation, a so-called thin film equation, that describes the evolution of the  
65 surface of a thin film subject to: i) viscous stresses, ii) a stabilizing Laplace  
66 pressure, and iii) a destabilizing disjoining pressure. The main qualitative  
67 features of the rupture in these nonlinear studies were similar to the ones in  
68 the linear analysis. Still, some quantitative differences were obtained con-  
69 cerning the breakup time in particular, that was found to be systematically  
70 inferior in the nonlinear studies compared to the linear analysis. This is likely  
71 due to the fact that the latter analysis underestimates the destabilizing effect  
72 of the long-range forces. Those various approaches were extended later to  
73 multilayer films [20, 29, 30].

74 The effect of a shear flow on a thin film rupture was first explored by  
75 Kalpathy et al. [31] for a liquid-liquid interface in a stratified flow and by  
76 Davis et al. [32] in a thin liquid film. They showed that when shear is  
77 imposed, the film rupture is delayed and that above a critical shear rate,  
78 the rupture is even suppressed. Beyond purely hydrodynamic explanations,  
79 another possible effect in practical systems could be the shear-induced mod-  
80 ification of the seed thermal fluctuations [33, 34].

81 In the present study, we investigate the impact of shear on the stability of  
82 a polymer thin film, using a numerical approach [35] inspired by Bertozzi  
83 and Zhornitskaya [36, 37]. In particular, by systematically studying various  
84 combinations of shear rates and Hamaker constants governing the intensity

85 of vdW forces, we discuss the existence of several regimes for the thin film  
 86 stability.

## 87 2. Problem position and model

### 88 2.1. Problem position

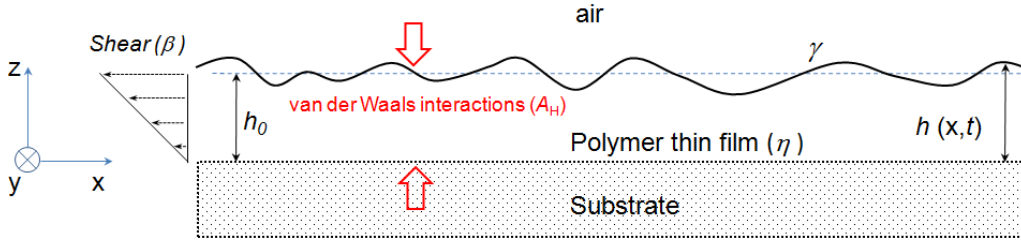


Figure 1: A viscous polymer film, of viscosity  $\eta$  and nominal thickness  $h_0$ , is placed atop a rigid substrate. External shear rate  $\beta$ , surface tension  $\gamma$  and van der Waals forces (with Hamaker constant  $A_H$ ) compete with each other, and generate a viscous flow that can either result in growth or damping of an initial interfacial perturbation. At horizontal position  $x$  and time  $t$  the film profile is  $h(x, t)$ . Invariance along  $y$  is assumed.

89 The problem studied is represented in Figure 1. A glassy polymer (such  
 90 as PS) thin film of nominal thickness  $h_0$  typically below 100 nm is lying on  
 91 a substrate and heated well above its glass transition temperature  $T_g$ . For a  
 92 PS film,  $T_g$  is about 100°C and the temperature of the study, similar to the  
 93 processing temperature, would be close to 200°C. At this temperature, the  
 94 polymer can be considered as a Newtonian fluid with a constant viscosity  
 95  $\eta_0$ , on the order of  $10^4$  Pa.s. The viscosity depends on molecular weight,  
 96 but the value indicated here is typical of polymers used in extrusion [14].  
 97 The surface tension of the polymer with air is noted  $\gamma$  ( $\sim 27.7$  mN/m for  
 98 PS at 200°C [38]) and the Hamaker constant for the substrate/polymer/air  
 99 system is noted  $A_H$ . The value of the latter is difficult to measure experi-  
 100 mentally, and though the typical order of magnitude of Hamaker constants  
 101 is similar for most systems, i.e.  $\sim 10^{-19}$  J, several values can be found  
 102 in the literature. For an air/PS/SiO<sub>2</sub> system, Seemann et al. [39] provide  
 103  $A_{H_{\text{air/PS/SiO}_2}} = 2.2 \cdot 10^{-20}$  J, similar to the value obtained using material re-  
 104 fractive indices and dielectric constants from the literature [40, 41]. In the  
 105 present study, to limit the numerical rupture time which increases with de-  
 106 creasing values of the Hamaker constant, we employ  $A_H$  to values between 5

107  $10^{-19}$  and  $5 \cdot 10^{-18}$  J. Shear, characterized by a shear rate  $\beta$ , is applied from  
 108 right to left. Different values of shear rates will be explored, and their effect  
 109 on an interfacial perturbation monitored through the evolution of the profile  
 110 thickness  $h(x, t)$  over time  $t$  and space along the  $x$ -axis.

## 111 2.2. Governing equation

112 Taking into account the previous considerations and a spatial invariance  
 113 along the horizontal direction  $y$ , the general thin film equation [21] is assumed  
 114 to describe the dynamics of the thickness profile  $h(x, t) = h_0 + \delta h(x, t)$ , where  
 115  $\delta h(x, t)$  is the perturbation field with respect to  $h_0$ . The thin viscous film  
 116 is experiencing Laplace and disjoining pressures, as well as shear stresses.  
 117 Neglecting gravitational forces, the thin film equation reads in our case:

$$\partial_t h + \frac{\gamma}{3\eta} \partial_x \left( h^3 \partial_x^3 h + \frac{3A_H}{6\pi\gamma h} \partial_x h \right) - \beta h \partial_x h = 0 . \quad (1)$$

118 Interfacial tension and viscosity are considered constant and possible  
 119 changes as a function of the film thickness are also neglected in this study.  
 120 To solve numerically the equation, one introduces the following dimensionless  
 121 variables and parameters:

$$\begin{aligned} H = \frac{h}{h_0} \quad ; \quad \Delta H = \frac{\delta h}{h_0} \quad X = \frac{x}{h_0} \quad ; \quad T = \frac{\gamma t}{3\eta h_0} \quad ; \quad \Lambda = \frac{\lambda}{h_0} \\ K = kh_0 = \frac{2\pi}{\Lambda} \quad ; \quad A = \frac{A_H}{6\pi\gamma h_0^2} \quad ; \quad B = \frac{3\eta\beta h_0}{2\gamma} , \end{aligned} \quad (2)$$

122 where  $\lambda$  is the wavelength of the initial harmonic perturbation (see below)  
 123 and  $k$  is the associated angular wavenumber. Note that both  $A$  and  $B$  depend  
 124 on the nominal film thickness and surface tension. The dimensionless thin  
 125 film equation can then be written as:

$$\partial_T H + \partial_X \left[ H^3 \left( \partial_X^3 H + 3AH^{-1} \partial_X H \right) \right] - 2BH \partial_X H = 0 . \quad (3)$$

126 The parameters of the study and the ranges over which they have been  
 127 varied are summarized in Table 1.

128

Parameters			Dimensionless parameters	
$h_0$	$A_H$	$\beta$	$A$	$B$
nm	J	$s^{-1}$		
[10–100]	$[5 \times 10^{-19} - 5 \times 10^{-18}]$	[0.2–200]	[0.001–0.1]	$[10^{-5} - 1]$

Table 1: Explored ranges for the parameters of the problem.

129 *2.3. Numerical method and boundary conditions*

130 The numerical procedure used here is a finite-difference method for thin-  
131 film flows [35]. Specifically, we aim at following the temporal and spatial  
132 evolution of an initial harmonic perturbation of wavelength  $\lambda$ . In contrast  
133 to previous studies (Davis et al. [32] or Kalpathy et al. [31]), we do not  
134 use periodic lateral boundary conditions here, but a large spatial window  
135 size instead. To optimize the computational time and to limit the artificial  
136 lateral boundary effects, we consider a truncated initial perturbation, with  
137 1.5 periods, completed at its edges by a flat profile. We impose flat conditions  
138 at the boundaries of the numerical domain. Finally, we have checked that  
139 the chosen number of periods at the center and the size of the spatial window  
140 do not affect the results.

141 At  $T = 0$ , the initial profile of the film is spatially discretized over  $M$   
142 segments, with a fixed spatial step  $\Delta X$  and a spatial index  $i \in [0, M - 1]$ , as:

$$H[\Delta X(i - i_0), 0] = 1 + \Delta H \cos[2\pi\Delta X(i - i_0)/\Lambda] , \quad (4)$$

143 where  $i_0$  is the index of the window center.

144 The numerical integration of Equation (3) along time  $T$  is then performed  
145 using a 4<sup>th</sup>-order Runge-Kutta scheme [35]. In order to be self-consistent  
146 with the lubrication framework and with the window-size constraint above,  
147 we impose the following scale separation:  $\Delta X \ll \Lambda \ll M\Delta X$ .

148 **3. Results**

149 *3.1. Linear stability analysis*

The effect of shear on the stability of a thin film can be estimated, as  
a first attempt, using a linear stability analysis. We stress that while such  
an approach allows one in principle to predict whether an infinitesimal dis-  
turbance at the surface is amplified or attenuated, it does not allow for the

quantitative study of rupture, which is outside the scope of linearity. We consider the evolution of an initial harmonic perturbation of small amplitude  $\Delta H_0$  around the nominal dimensionless thickness of the film (equals to 1). The perturbative field  $\Delta H$  comprises a time-dependent factor  $e^{\Gamma T}$ , where  $\Gamma$  is the growth rate of the perturbation (the perturbation is amplified if  $\Gamma > 0$  and damped if  $\Gamma < 0$ ) and a space-dependent oscillatory factor  $e^{iKX}$ :

$$H = 1 + \Delta H \tag{5a}$$

$$\Delta H = \Delta H_0 e^{\Gamma T} e^{iKX} . \tag{5b}$$

150 This leads, after substitution in Equation (3), to the following dispersion  
151 relation:

$$\Gamma = K^2(3A - K^2) + 2BiK . \tag{6}$$

152 The growth rate of the perturbation is a complex number, with a real  
153 part  $\Gamma_R$  and an imaginary part  $\Gamma_I$ . The real part evaluates the actual rate at  
154 which the perturbation is amplified or damped. It appears to be independent  
155 of the shear and thus coincides with the solution of the no-shear case, *i.e.*  
156 for  $B = 0$  (see [25, 28]). A consequence of such a feature is that a numerical  
157 treatment of the non-linear (*i.e.* beyond linear analysis) thin film equation  
158 will be needed in order to understand further the potential role of shear  
159 in the dewetting process. The evolution of  $\Gamma_R$  as a function of  $K$ , obtained  
160 from Equation (6), is shown in Figure 2 and compared to numerical solutions  
161 of Equation (3), for different values of  $A$ , including ones outside the range  
162 studied later on with shear. It can be seen that in all cases the numerical  
163 results are self-consistently in quantitative agreement with the analytical  
164 prediction. Besides, one observes a maximum  $\Gamma_{\max} = \Gamma(K_{\max})$ , defined by:

$$K_{\max} = \sqrt{\frac{3A}{2}} \tag{7}$$

$$\Gamma_{\max} = \frac{9}{4} A^2 .$$

165 Note that the wavelength  $\Lambda_{\max} = 2\pi/K_{\max}$  of this fastest growing mode will  
166 be used as a wavelength  $\Lambda$  in all numerical computations below, in order to  
167 reduce the total computational time.

168 Due to the imaginary part  $\Gamma_I$ , the perturbation is transported and shifted  
169 in the shear direction. This shift is explicitly highlighted when injecting  
170 Equation (6) into Equation (5), leading to:

$$\Delta H = \Delta H_0 e^{\Gamma_R T} e^{iK(X+2BT)} . \tag{8}$$



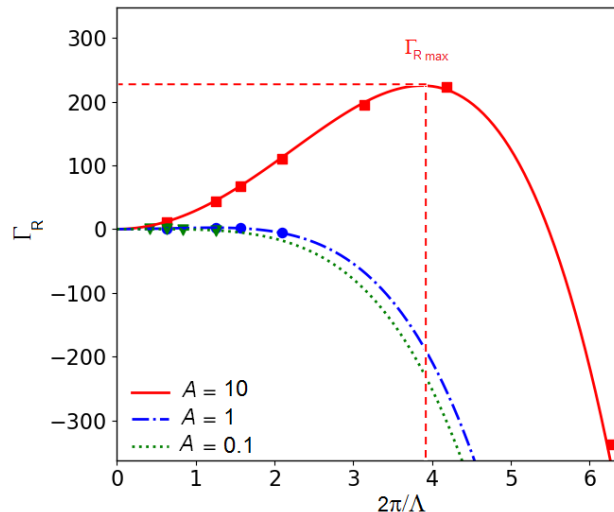


Figure 2: Real part  $\Gamma_R$  of the growth rate of the perturbation as a function of the angular wavenumber  $K = 2\pi/\Lambda$ , as obtained from Equation (6) (lines), as well as from numerical solutions of Equation (3) (symbols), for different values of the dimensionless Hamaker constant  $A$ , as indicated.

171 Thus, the perturbation propagates along  $-X$  (i.e. the shear direction) with  
 172 a speed equal to  $2B$ .

### 173 3.2. Rupture without shear

174 Here, an initial harmonic perturbation with an amplitude  $\Delta H_0 = 0.1$  is  
 175 considered, and Equation (3) is solved with  $B = 0$ . Due to vdW forces,  
 176 the film may undergo a possible rupture after a time which depends on the  
 177 value of the dimensionless Hamaker constant  $A$ . Since the numerical scheme  
 178 is only stable for strictly positive  $H$  values, a criterion for rupture has been  
 179 set as the time  $T_R$  at which the spatial minimum of  $H$  reaches 0.1. We have  
 180 checked that other small-enough values of this arbitrary threshold do not  
 181 change qualitatively the results.

182 A typical evolution of the film profile is given in Figure 3 for  $A =$   
 183 0.01. It is seen that the amplitude of the interfacial perturbation increases  
 184 monotonously over time, until the film ruptures (at  $T_R = 4800$  in this case,  
 185 with our criterion above).

186 We now turn to the detailed study of the rupture time. First, the ef-  
 187 fect of the initial amplitude of the perturbation is presented in Figure 4a for

188 different values of  $A$ . Apart from a numerical prefactor of order unity, the de-  
 189 crease of the dimensionless rupture time  $T_R$  with increasing initial amplitude  
 190  $\Delta H_0$  as measured from our numerical solutions follows the linear-stability  
 191 extrapolation law proposed by Sharma [27]:

$$T_R = \frac{1}{\Gamma_{\max}} \ln \left( \frac{1}{\Delta H_0} \right) . \quad (9)$$

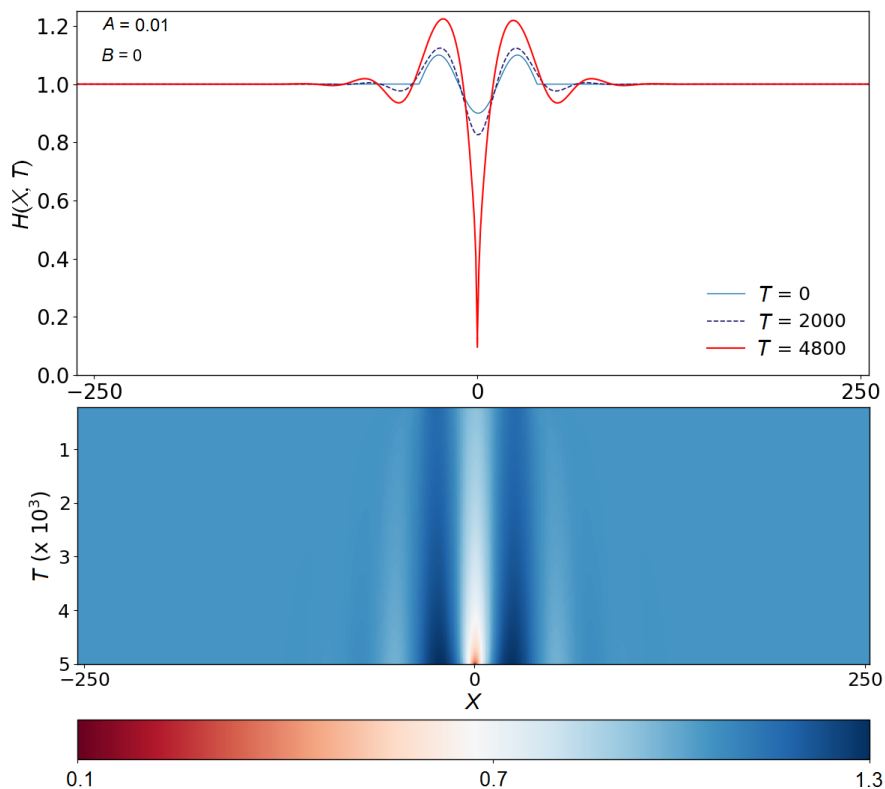


Figure 3: (top) Film profiles  $H(X, T)$  versus the horizontal position  $X$ , at three different times  $T$  as indicated, as obtained from the numerical solution of Equation (3) with  $A = 0.01$  and  $B = 0$ , for an initial harmonic perturbation with  $\Delta H_0 = 0.1$  and  $\Lambda = \Lambda_{\max}$ . (bottom) Spatiotemporal diagram of the interfacial evolution, with  $X$  and  $T$  as axes, and the magnitude of  $H$  represented using the color code indicated below.

192 We stress that the expression predicted by Sharma is equivalent to the  
 193 one by Ruckenstein [25] provided that  $\Delta H_0 = 1/e$ . Indeed, the expression of  
 194 Ruckenstein corresponds by definition to the time constant of the exponen-  
 195 tial growth and is therefore independent of  $\Delta H_0$ . Similarly, Ruckenstein's

196 expression is similar to the one predicted by Vrij [23], the two expressions  
 197 quantitatively differing by a factor 2 only. These three theoretical estimates  
 198 of  $T_R$  come from a similar linear approximation, and differ only by the exact  
 199 convention chosen.

200 Putting back dimensions, Equation (9) is equivalent to:

$$t_R = \frac{48\pi^2\gamma\eta h_0^5}{A_H^2} \ln\left(\frac{h_0}{\delta h_0}\right), \quad (10)$$

201 where  $\delta h_0$  is the initial amplitude of the perturbation.

202 As a guide for practical purposes, and using the values of the physical param-  
 203 eters  $\eta$  and  $\gamma$  provided above, the rupture time  $t_R$  is plotted in Figure 4b as  
 204 a function of the ratio  $h_0^5/A_H^2$ , with real units, for the case where  $\delta h_0/h_0=0.1$ .

205 Apart from the numerical prefactor of order unity already mentioned  
 206 above, it appears that Sharma's prediction describes well the data over 10  
 207 decades. This suggests that non-linear effects are not essential to understand  
 208 the main qualitative features of the film rupture process – under no shear.

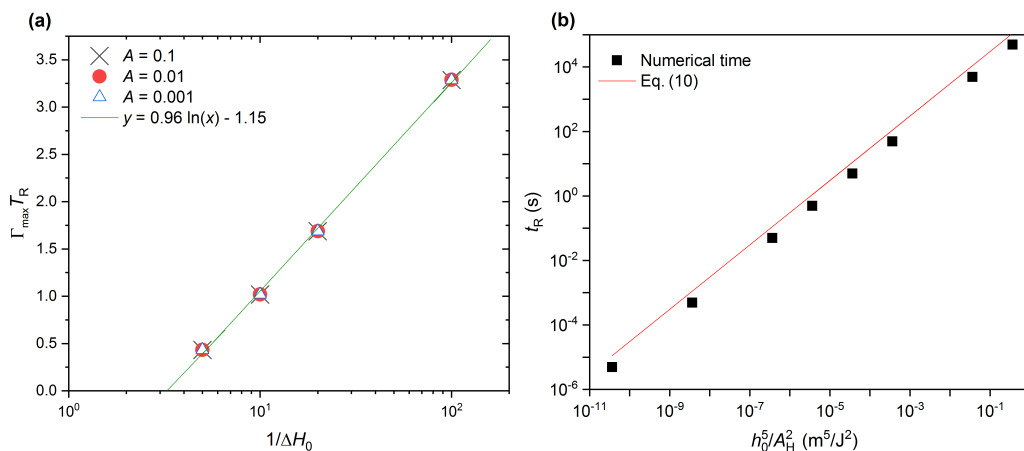


Figure 4: (a) Dimensionless rupture time  $T_R$  as a function of the inverse of the dimensionless perturbation amplitude  $\Delta H_0$ , for different values of the dimensionless Hamaker constant  $A$ . The solid line is a best fit to Eq. (9). (b) Dimensioned version of the rupture times obtained for  $\delta h_0/h_0=0.1$  in panel a) with the values of interest presented in Table 1. The solid line is Eq. (10).

209 *3.3. Effects of shear*

210 *3.3.1. Influence of the shear rate*

211 Various finite shear rates ( $B \neq 0$ ) have been tested within the same nu-  
 212 merical framework as the one described above. The low-shear-rate behavior  
 213 ( $B \ll A$ ) is presented in Figure 5a, while the high-shear-rate behavior ( $B$   
 214  $\gg A$ ) is presented in Figure 5b. Over time, the perturbation moves along  
 215 the  $x$ -axis in the direction in which the shear is applied, from right to left.  
 216 At low shear rates, the behavior is similar to what is observed without shear:  
 217 the perturbation grows with time and eventually leads to film rupture. At  
 218 high shear rates, however, the perturbation is damped, leading to what could  
 219 be described as a healing of the interface (*i.e.* going back to an unperturbed  
 220 flat initial state) at long times.

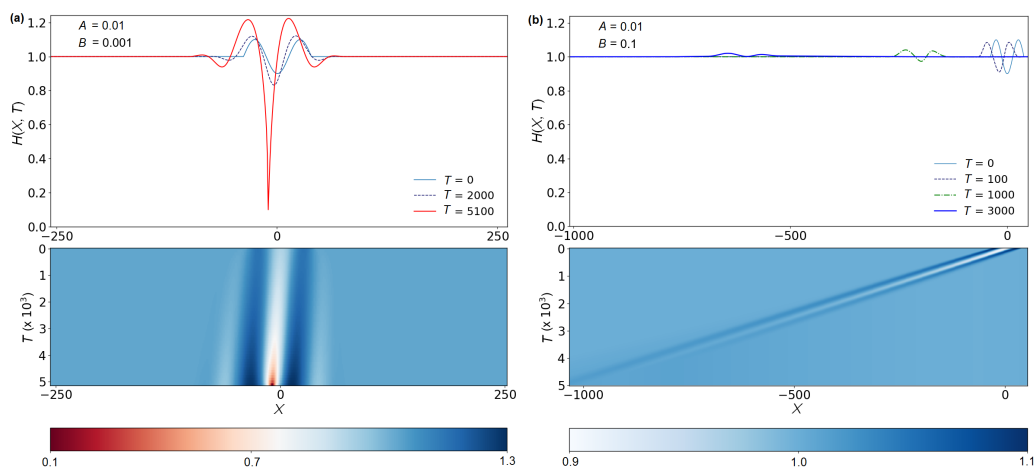


Figure 5: (top) Film profiles  $H(X, T)$  versus the horizontal position  $X$ , at three different times  $T$  as indicated, as obtained from the numerical solutions of Equation (3) with  $A = 0.01$ , for an initial harmonic perturbation with  $\Delta H_0 = 0.1$  and  $\Lambda = \Lambda_{\max}$ . The dimensionless shear rates are fixed to  $B = 0.001$  and  $B = 0.1$ , in panels (a) and (b) respectively. (bottom) Corresponding spatiotemporal diagrams of the interfacial evolutions, with  $X$  and  $T$  as axes, and the magnitude of  $H$  represented using the color codes indicated below.

221 *3.3.2. Critical shear rate*

222 To understand more quantitatively the effect of shear on the perturbed  
 223 interface profile, the maximum  $H_{\max}$  and minimum  $H_{\min}$  of the latter are  
 224 plotted in Figure 6 as functions of time, and for different shear rates. At low

225 shear rate, it is seen that the time of rupture increases compared to the case  
 226 without shear. At high shear rate, healing is confirmed by the fact that both  
 227 extrema converge to 1, *i.e.* towards the flat-interface situation.

228

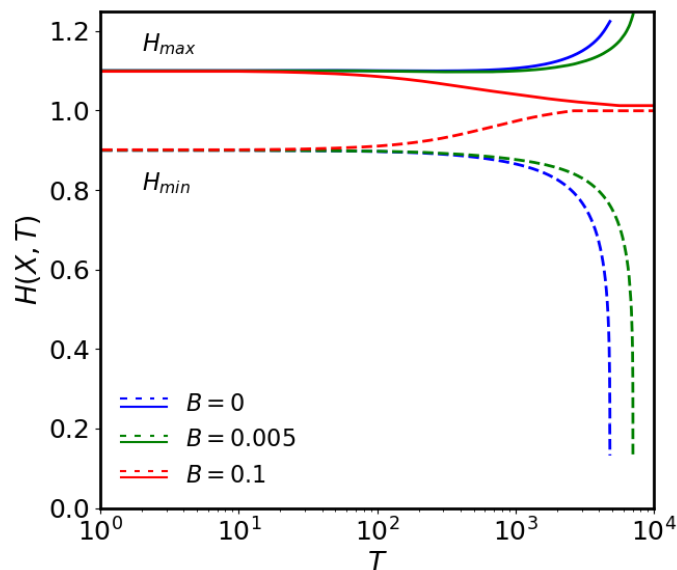


Figure 6: Temporal evolution of the maximum ( $H_{\max}$ ) and minimum ( $H_{\min}$ ) values of the dimensionless film profile, for three applied dimensionless shear rates,  $B = 0, 0.005, 0.1$ , as obtained from numerical evolutions such as the ones in Figure 5.

229 It is now interesting to examine what happens at intermediate shear rates,  
 230 *i.e.*  $B$  close to  $A$ . Typical results are presented in Figure 7. Here, over the  
 231 total computational time, no rupture is observed, but no healing either. As  
 232 seen in the inset, the evolution of the perturbation, characterized as in Figure  
 233 6, is not monotonic, suggesting the existence of a transient regime where vdW  
 234 forces and shear compete with each other over times longer than the total  
 235 time computed.

236 We now investigate the influence of shear on the film rupture. Figure 8  
 237 shows the dimensionless rupture time  $T_R$  as a function of the dimensionless  
 238 shear rate  $B$ . For low shear rates, the rupture time is only slightly higher  
 239 than the value without shear. Then, for values of  $B$  higher than  $\sim 0.005$ ,  $T_R$   
 240 increases sharply, and becomes higher than the total computational time for  
 241  $B > 0.014$ . For  $B > 0.03$ , perturbation damping and healing of the interface  
 242 are observed. A so-called "transient regime" is observed for  $0.014 < B <$

243 0.03. A similar trend was found in a previous numerical simulation (Davis  
 244 *et al.* [32]) using periodic boundary conditions with a coarse calculation  
 245 domain. Specifically, Davis *et al.* [32] observed that the rupture is suppressed  
 246 for  $B \approx 10A$ . The current systematic study allows us to construct a novel  
 247 phase diagram, exhibiting in particular: i) perturbation damping for values  
 248 as low as  $B = 3A$ ; ii) the existence of a narrow transient regime with a non-  
 249 monotonic variation of the interface profile along time, resulting in neither  
 250 rupture nor healing within the accessed temporal and spatial window.

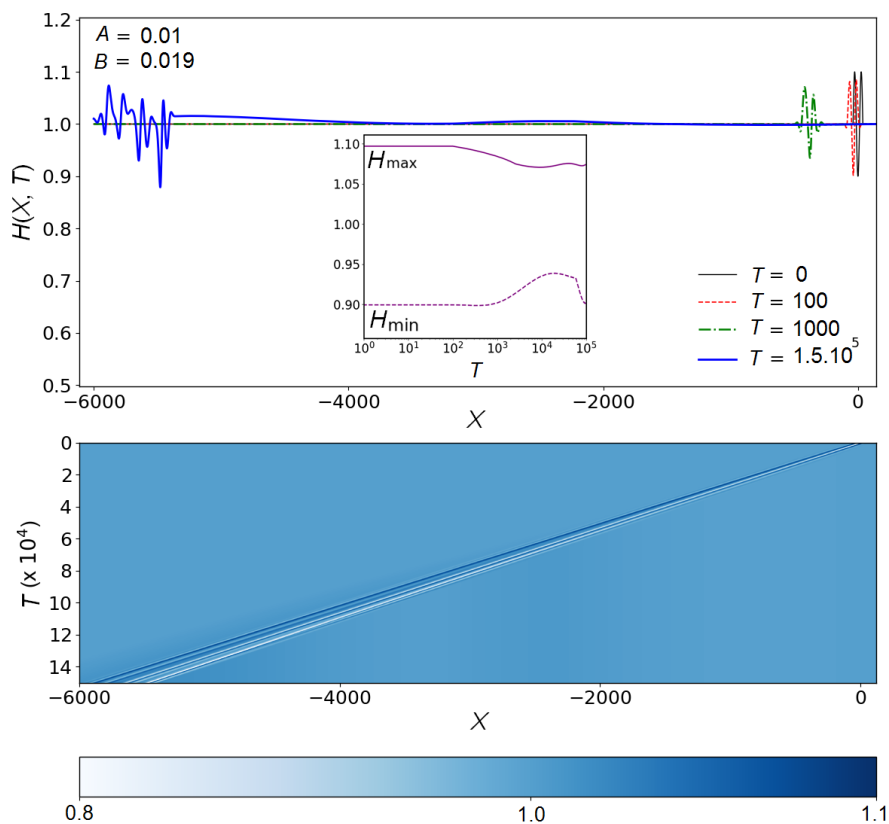


Figure 7: (top) Film profiles  $H(X, T)$  versus the horizontal position  $X$ , at four different times  $T$  as indicated, as obtained from the numerical solution of Equation (3) with  $A = 0.01$  and  $B = 0.019$ , for an initial harmonic perturbation with  $\Delta H_0 = 0.1$  and  $\Lambda = \Lambda_{\max}$ . Inset: temporal evolutions of the profile's extrema, as in Figure 6. (bottom) Corresponding spatiotemporal diagram of the interfacial evolution, with  $X$  and  $T$  as axes, and the magnitude of  $H$  represented using the color code indicated below.

251

252 Interestingly, a natural dimensionless critical shear rate  $B_c$  can be identi-  
 253 fied in the model. Indeed, by balancing the Hamaker and shear contributions  
 254 in Equation (3), recalling that we have set  $K = K_{\max}$ , and invoking Equa-  
 255 tion (7), one gets:

$$B_c \sim 3AK \sim 3\sqrt{\frac{3}{2}}A^{3/2}. \quad (11)$$

256 For  $A = 0.01$ , the latter estimate gives  $B_c \approx 0.0037$ , which corresponds  
 257 approximately to the onset value of  $B$  in Figure 8 after which  $T_R$  sharply  
 258 increases with  $B$ .

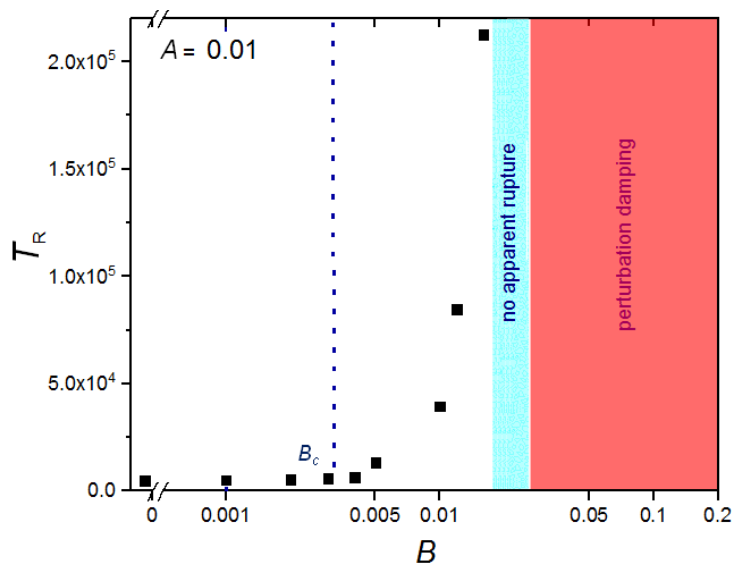


Figure 8: Dimensionless rupture time  $T_R$  as a function of the dimensionless applied shear rate  $B$ , for a dimensionless Hamaker constant  $A = 0.01$ . When  $T_R$  becomes larger than the total computational time, no rupture is observed, and for large enough  $B$  healing of the profile is even observed, as summarized by the colored areas. The vertical dashed line indicates  $B_c \approx 3.7 \cdot 10^{-3}$ , according to Equation (11).

259 The study above can be reproduced for several values of  $A$ . A similar  
 260 trend is systematically recovered (not shown). Furthermore, a master curve  
 261 is obtained in Figure 9, when plotting the ratio of the rupture time with shear  
 262 and the rupture time without shear as a function of the ratio  $B/A$ . First, we  
 263 recover the monotonic increase of the rupture time with shear rate. Secondly,  
 264 the master rescaling is expected if, near a rupture event, one neglects the

265 capillary Laplace contribution over the Hamaker one in Equation (3), divide  
 266 the whole equation by  $A$ , and absorb  $A$  in the definition of time.

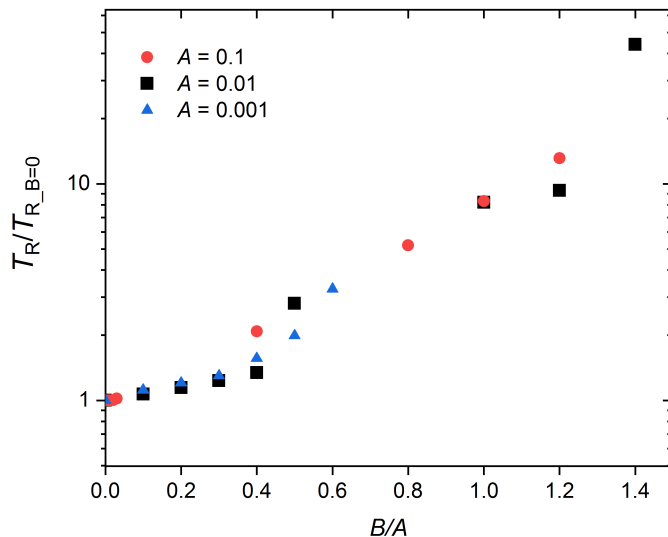


Figure 9: Rupture time rescaled with the no-shear rupture time as a function of the ratio between dimensionless shear rate  $B$  and dimensionless Hamaker constant  $A$ , for different values of  $A$ , as indicated.

267 Finally, let us discuss the layer stability in nanolayer coextrusion, from  
 268 the results obtained here. In our study [14] on a PS/PMMA multilayer  
 269 system, we made the hypothesis that rupture in multilayer films is induced  
 270 by thermal fluctuations of amplitude  $\sqrt{k_B T / \gamma} \sim 10^{-9}$  m (where  $k_B$  is the  
 271 Boltzmann constant) [42] at the interface between adjacent layers, that are  
 272 then amplified by vdW forces. Balancing capillary forces with vdW ones, the  
 273 critical thickness was defined as:

$$h^* \sim \left( \frac{A_H}{3\pi\gamma} \right)^{1/2}. \quad (12)$$

274 Using  $A_H \sim 10^{-18}$  J [40] and  $\gamma \sim 1$  mN/m [43], we obtained  $h^* \sim 10^{-8}$   
 275 m, in good agreement with our experimental observations.

276 In the present study, we showed that rupture can be suppressed for  $B \sim$   
 277  $3A$ . Assuming that our simple model can be employed in the case of a



278 multilayer system too, and putting back dimensions through Equation (2),  
279 we get a critical shear rate for rupture suppression:

$$\beta_s \sim \frac{A_H}{3\pi\eta h_0^3}. \quad (13)$$

280 Using  $h_0 \sim h^*$  and the values of the physical parameters provided above,  
281 we obtain  $\beta_s \approx 10 \text{ s}^{-1}$ . Interestingly, the latter value is typical of shear rates  
282 occurring during nanolayer coextrusion [44]. Since  $\beta_s$  decreases rapidly as  $h_0$   
283 increases, it may explain why stable layers with thicknesses as small as 20 nm  
284 can be formed via this process – despite a processing time ( $\sim 1 \text{ min}$ ) much  
285 larger than the rupture times predicted by Vrij, Ruckenstein and Sharma in  
286 a no-shear situation ( $\sim 1 \text{ s}$ , see equation 10).

#### 287 4. Conclusion

288 We have developed a numerical model to study the effect of shear on  
289 the stability of an ultra-thin polymer film, taking into account capillary and  
290 vdW forces. We identified three regimes: i) a rupture regime at low shear  
291 rates, with a rupture time systematically larger than the one in the no-shear  
292 case, the latter being in agreement with the expressions predicted by Vrij,  
293 Ruckenstein and Sharma; ii) a transient regime in which shear and Hamaker  
294 forces compete with each other over the whole time window, leading to a  
295 non-monotonic temporal variation of the perturbed interface; iii) a regime  
296 at high shear rates in which shear suppresses rupture: a perturbed interface  
297 will evolve towards a flat interface over time. Interestingly, while a linear  
298 analysis is sufficient to describe the rupture time in the absence of shear,  
299 the nonlinearities appear to be crucial in presence of moderate shear. This  
300 study paves the way to a better analysis and control of the stabilizing and  
301 destabilizing effects in nanocoextrusion processes.

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