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Dewetting of thin polymer films at temperatures close to the glass transition

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Abstract. We present detailed studies on dewetting of thin polystyrene (PS) films which were deposited onto silicon wafers coated with a polydimethylsiloxane (PDMS) monolayer. Experiments were performed at temperatures close to the glass transition temperature of PS. Several significant deviations from the dewetting behaviour of Newtonian liquids were observed. The length of the PS molecules, and thus the viscosity, turned out to be of minor importance in determining the dewetting velocity, in particular for the later regimes. In stark contrast, the geometry of the drying spot had a striking influence on the dewetting velocity. Initially, dewetting from straight contact lines proceeded faster than the opening of circular holes. At later stages, the process slowed down significantly in both cases. Under the conditions at which our experiments were performed, PS cannot flow like a simple liquid. Thus, the observed dewetting has to be the consequence of plastic deformation induced by capillary forces. Our results indicate that under such conditions the energy dissipation process is strongly affected by geometry, which is not the case for viscous liquids.

PACS. 68.60.-p Physical properties of thin films, nonelectronic – 61.41.+e Polymers, elastomers, and plastics – 68.55.-a Thin film structure and morphology – 83.50.-v Deformation and flow

1 Introduction

If a liquid is forced to cover a substrate which it does not want to wet, it will retract from this substrate, *i.e.* the liquid will dewet the surface. The origin for this behavior is found in the capillary driving force acting at the three-phase contact line. This force is the result of an imbalance between the three interfacial tensions of the liquid-air, liquid-substrate, and substrate-air interfaces which meet at this contact line. The capillary force is related to the contact angle, which is formed at the contact line between the tangent to the liquid surface and the plane of the substrate. Typically, for a positive liquid-substrate interfacial tension, dewetting is observed when the liquid has a higher surface tension than the substrate: In this case, it is energetically favorable to remove the liquid. Even if initially the liquid is forced to cover the substrate homogeneously (for example, by the spin-coating process), such a liquid film is not stable and eventually a three-phase contact line will be formed. This contact line can either result from a nucleation process or an intrinsic instability of the film (*i.e.* spinodal dewetting). Once the contact line is formed, dewetting starts and the removed liquid is collected in a rim just ahead of the moving contact line. It is important to realize that the capillary force is acting independently of the state of the liquid. Thus, even if the liquid is vitrified, a force is pushing the glassy film as long as the system is not at equilibrium. Dewetting, however, may be stopped, at least on experimentally accessible times scales, because this acting force may be too weak to push a vitreous solid or a highly viscoelastic material.

Dewetting of thin polymer films has been studied extensively [1–7] and until rather recently results have been exclusively interpreted considering the polymer as a viscous liquid. Although a polymer melt is characterized also by an elastic modulus, analysis of the dewetting process based on such assumption works surprisingly well in most cases. The importance of elastic contributions was discussed theoretically first by Safran and Klein [8] who proposed that intrinsically unstable thin films of a Newtonian liquid may be stabilized by an elastic component. Experimental work by Debregeas *et al.* [9,10] demonstrated, for high molecular-weight polymers, that holes can open without the formation of a rim. Seemann *et al.* [11] analysed the shape of dewetting rims and concluded that viscoelastic effects are responsible for asymmetric shapes of the

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rim. In a series of dewetting experiments with almost glassy polystyrene films even more asymmetric shapes were found by Reiter [12]. More importantly, since polymers covering a wide range of molecular weights were used, viscosity did not seem to be the most dominating factor anymore. These experiments have initiated several theoretical works [13–16]. Various mechanisms have been proposed to explain the observed highly asymmetric shape of the rim. Asymmetry may be the consequence of a strong elastic component [16], the result of strain hardening [15] or due to shear thinning behavior of the polymer material forming the rim [13,14]. Interestingly, although the basic assumptions are quite different, all approaches are able to reproduce asymmetric shapes of the rim as observed in experiments.

In this work, we extend our previous studies [12] to longer times, to thicker films, and to different temperature regimes. More detailed information will be presented in particular on the time evolution of hole opening. In addition, we compare the behavior of a circular geometry as given by dewetting from a point-like starting point with observations of dewetting from an extended straight three-phase contact line, as it is the case when the film is retracting from the edge of the sample.

2 Experimental section

We used, as in our previous study [12], thin polystyrene (PS) films on top of silicon substrates coated with polydimethylsiloxane (PDMS) layers. We used two molecular weights (weight average: M_w) for the PS. M_w = 125 kg/mol and an index of polydispersity I_p (as defined by the ratio of the weight average and number average (M_n) molecular weight) of I_p = 1.02 and M_w = 3900 kg/mol, I_p = 1.05. The polymers were purchased from PSS, Mainz/Germany. In this paper, we identify the two PS by PS125k and PS3900k, respectively. The film thickness was varied between 10 and 120 nm, as measured by ellipsometry. The bulk glass transition temperature of polystyrene is about 105 °C. The PDMS coatings were: a) end-grafted layers (polymer brushes) of SiH-terminated PDMS molecules (PDMS78k: M_w = 78 kg/mol, I_p = 1.07 and PDMS127k: M_w = 127 kg/mol, I_p = 1.05) or b) layers of adsorbed PDMS (PDMS38k: M_w = 38.3 kg/mol, I_p = 2.56 with layer thickness about 7 nm and PDMS80k: M_w = 80.5 kg/mol, I_p = 2.14 with layer thickness about 10 nm). The irreversibly adsorbed layers were obtained by annealing the spin-coated films on hydroxilated (UV-ozone treated) silicon wafers at 150 °C for 5 hours under vacuum [17]. PS films were prepared from toluene solution spin-coated directly onto the PDMS-coated Si-wafers. Dewetting of PS films thicker than 20 nm was studied in real time by using optical microscopy. Annealing was performed *in situ* in the temperature range between 107 °C and 140 °C. We followed either the opening of a circular hole or the displacement of a straight three-phase contact line, which was created by breaking the sample in two parts, a process used previously [18]. The dewetting velocity $V(t_i)$ was determined by taking differences,

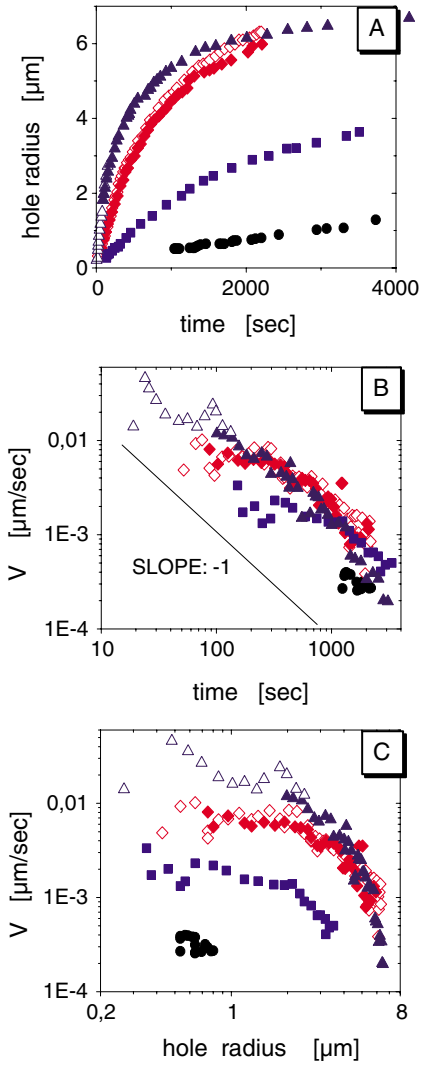

Fig. 1. Opening of a hole in a 64 nm thick PS3900k film on a grafted PDMS127k layer of 22 nm at different temperatures (Circles: 120 °C, squares: 125 °C, diamonds: 130 °C, and triangles: 140 °C). Open and full symbols represent independent measurements on the same sample. A) Hole radius as a function of elapsed time on linear scales. B) and C) for the same data, dewetting velocity V as a function of time and hole radius, respectively, on logarithmic scales.

$V(t_i) = (d(t_i) - d(t_{i-1}))/(t_i - t_{i-1})$, where $d(t_i)$ is the dewetted distance at time t_i.

3 Results and discussion

3.1 The influence of temperature and molecular weight on dewetting

In Figure 1, we show some representative curves for the opening of a circular hole in films of the higher molecular-weight polystyrene (PS3900k). These measurements demonstrate an unexpected evolution of the dewetting behavior for PS films on highly non-wettable PDMS

substrates close to the glass transition temperature of PS. The first surprising observation is that the growth of the hole diameter (Fig. 1A) cannot be represented by a simple power law behavior as it is the case for the dewetting for viscous liquids [1]. It also does not follow an exponential increase with time, as it is found, *e.g.*, for the viscous bursting of polymer films on a liquid substrate [9]. Based on our observations, it seems necessary to distinguish different regimes of the dewetting process. The initial stages of hole formation and building-up of the rim were followed by a section of almost constant dewetting velocity. However, already for holes of only a few micrometers in diameter, the dewetting velocity started to decrease almost linearly in time (see the slope -1 plotted in Fig. 1B). Such a drastic slowing-down leads to the impression that dewetting comes to a standstill at a hole radius of about 10 micrometers (see Fig. 1A). As it was experimentally difficult to measure velocities below $10^{-4}\,\mu$m/s, it is not clear if the linear decrease in time continued at later stages or if the velocity decreased even more rapidly. Some curves indicate such an accelerated slowing-down for hole diameters larger than about 10 micrometers.

A second surprising observation is shown Figure 1B. Although the opening velocity of the holes was significantly different at short times (*e.g.*, 100 s) all dewetting velocities were about the same at later times ($\sim$ 1000 s) when the hole radii of $\sim 5\,\mu$m were reached. To some extent, this reflects the logarithmic time dependence for the opening of the hole. In addition, a small initial opening velocity at low temperatures implies that some minutes are needed before the hole becomes visible under an optical microscope. The hole diameter has to be larger than about 0.5 microns. Thus, for a dewetting velocity $V = 0.0005\,\mu$m/s (and assuming that V is constant), $\sim$ 1000 seconds are needed before a dewetting velocity can be determined experimentally, with the consequence that for low-temperatures data points are detectable at rather late times. (For the same reason the uncertainty in determining the exact starting point ($t = 0$) of the dewetting process increases at low dewetting velocity.)

A third unexpected result is that, independent of temperature, dewetting apparently came to a standstill once the hole has reached a radius of about 8 μm (see Fig. 1C). It seems that the capillary driving forces are not strong enough to create holes of larger diameter. We note that this diameter varied between samples but was always of the order of some ten micrometers. This variation could be related to the properties of the underlying PDMS brush. These brush properties may also have some influence on the initial opening velocity.

In the dewetting of purely viscous liquids such stopping of dewetting is not expected [19]. The energy resulting from the capillary driving forces is mostly dissipated in a small wedge close to the contact line. In such a case, the dewetting velocity is constant and the holes continue to grow until the whole sample is dewetted. The dewetting velocity may decrease, however, in the presence of slippage at the liquid-substrate interface. In this case, energy is dissipated over the whole length of the moving part

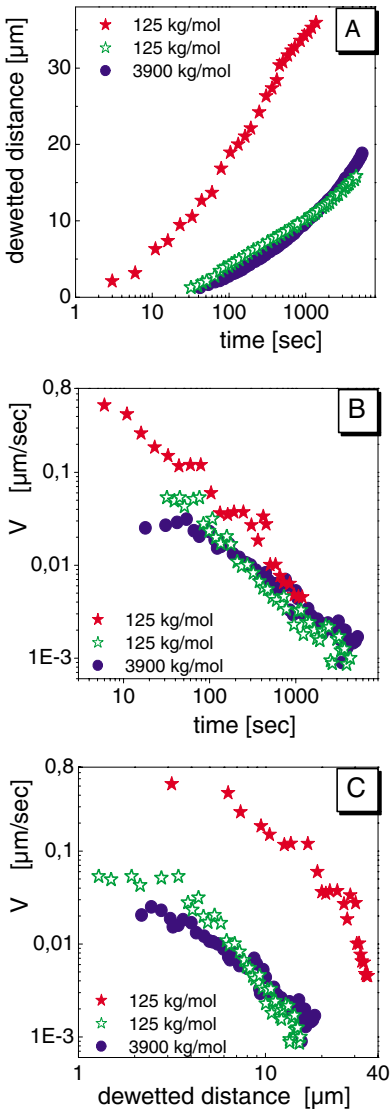

Fig. 2. Dewetting at 120 °C from the edge (straight line) of the silicon wafer supporting a 63 nm thick PS3900k film (circles) on an adsorbed PDMS38k layer of 7 nm. This behavior is compared to a 55 nm thick PS125k film (open stars) on an adsorbed PDMS80k layer of 11 nm and a 84 nm thick PS125k film (full stars) on a grafted PDMS78k layer of 17 nm. A) Dewetted distance (linear scale) as a function of elapsed time (logarithmic scale). B) and C) For the same data, dewetting velocity V as a function of time and dewetted distance, respectively, on logarithmic scales.

(the rim). As the width of the rim grows with time, the constant driving capillary forces have to push an increasingly larger rim and thus the dewetting velocity will slow down with time, but only weakly ($V \sim t^{-1/3}$ [18,19]). The much faster decrease of V with time found in the present experiments is thus a special feature of dewetting of quasi-solid films. At present, the mechanism responsible for this behavior is not yet clear.

One might think that the length (the molecular weight) of the polymers used may be an important parameter determining the dewetting velocity. In the case of

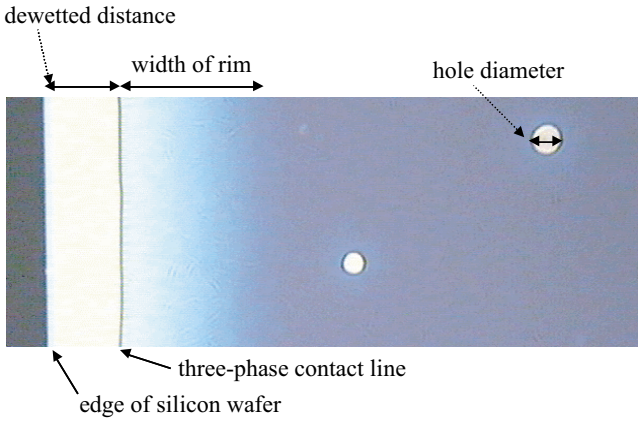

Fig. 3. Optical micrograph of a 80 nm thick PS125k film on a grafted PDMS78k layer of 17 nm after dewetting at 130 °C for 100 s. Size of the image: $40 \times 100\,\mu m^2$.

polymeric liquids with low elastic modulus, the dewetting velocity is inversely proportional to the viscosity [1,18,19]. For the two polymers used (PS3900k and PS125k), the intrinsic viscosity (determined at temperatures far above the glass transition) differs by about a factor of 10^5. However, as we show in Figure 2 for dewetting from an edge, at temperatures close to the glass transition (120 °C in this example) the difference in V is almost negligible. In most cases though, at least at the beginning, V is faster for PS125k than for PS3900k. However, the exact value of V may also depend on other parameters like the properties of the underlying substrate coated with a PDMS layer (in Fig. 2 we give an example). More detailed studies are necessary to elucidate this point. It is, however, already clear that the viscosity of the PS film is not the only parameter determining V. As seen here and also in [12], during some regimes of dewetting the same values of V may be obtained, independent of viscosity. On the other hand, as there are regimes where V depends, *e.g.*, on temperature, the viscosity has some influence on dewetting.

Considering the influence of the film thickness, we do have some indications that at the beginning thinner films dewet faster than thicker ones. On the other hand, we also found that, for films of identical thickness, V could differ initially by up to a factor of 10. Since we do not have yet sufficient information concerning the other possible parameters which may affect the dewetting process, we cannot give a definite answer on the dependence of V film thickness. We would like to recall that interfacial properties controlled by conformational parameters of the PDMS coating have a strong influence in dewetting of PDMS on PMDS coatings (see, *e.g.*, [18]). Thus, taking into account that the exact mechanism of energy dissipation is still unknown in the present case, one may anticipate that small difference in the properties of the PDMS coating may also be responsible for the observed differences between films on variously coated substrates.

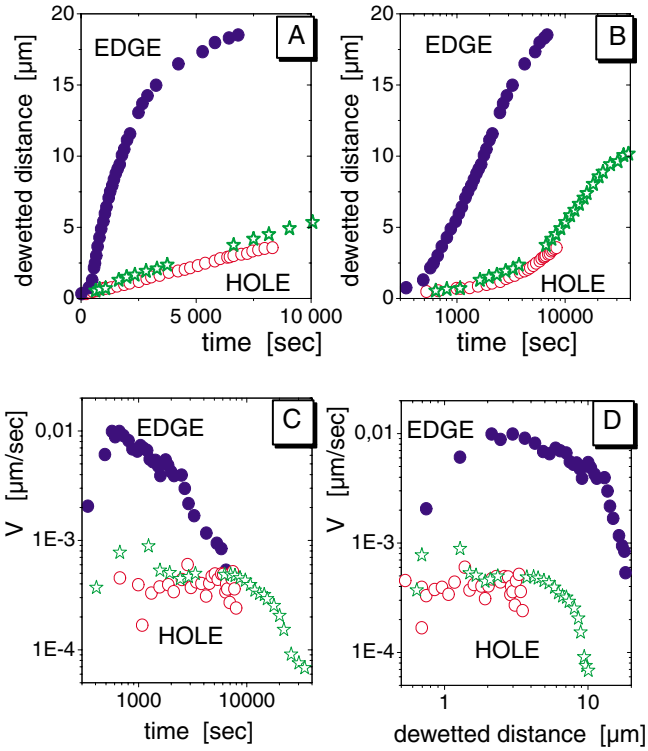

Fig. 4. Comparison of dewetting at 110 °C of PS125k films on a grafted PDMS78k layer of 17 nm, from the edge (full symbols) and corresponding opening of a hole (open symbols). The PS film thickness is 63 nm for the circles and 83 nm for the stars. A) Dewetted distance as a function of time on linear scales. B) The same data as in A) but on a logarithmic time scale. C) and D) for the same data, dewetting velocity V as a function of time and dewetted distance, respectively, on logarithmic scales.

3.2 The influence of the dewetting geometry: straight line vs. circular hole

The most surprising observation, however, is that, very much in contrast to viscous liquids, the geometry of the dewetting experiment has an influence for the highly elastic (quasi-solid) films studied here. As we have shown in Figures 1 and 2, the opening of a hole (Fig. 1) and the retraction of a straight dewetting front from the edge of the sample (Fig. 2) show a qualitatively similar behavior. However, a quantitative comparison on the same sample indicates significant differences (see Figs. 3 and 4). Figure 3 shows the opening of a hole and the retraction of a straight line from the edge of the sample, observed simultaneously on a single sample: it is clear that the dewetting behavior is different. At least initially, the retraction from the edge is significantly faster than the opening of holes. At later times, however, the extrapolation of the velocity for dewetting from an edge and the decrease of dewetting velocity of a hole are superposed (see Fig. 4C).

Figure 4 also shows that in both cases the dewetting velocity eventually decreases significantly. However, in the case of the opening of a circular hole, it exists a distinct interval of almost constant velocity before the velocity

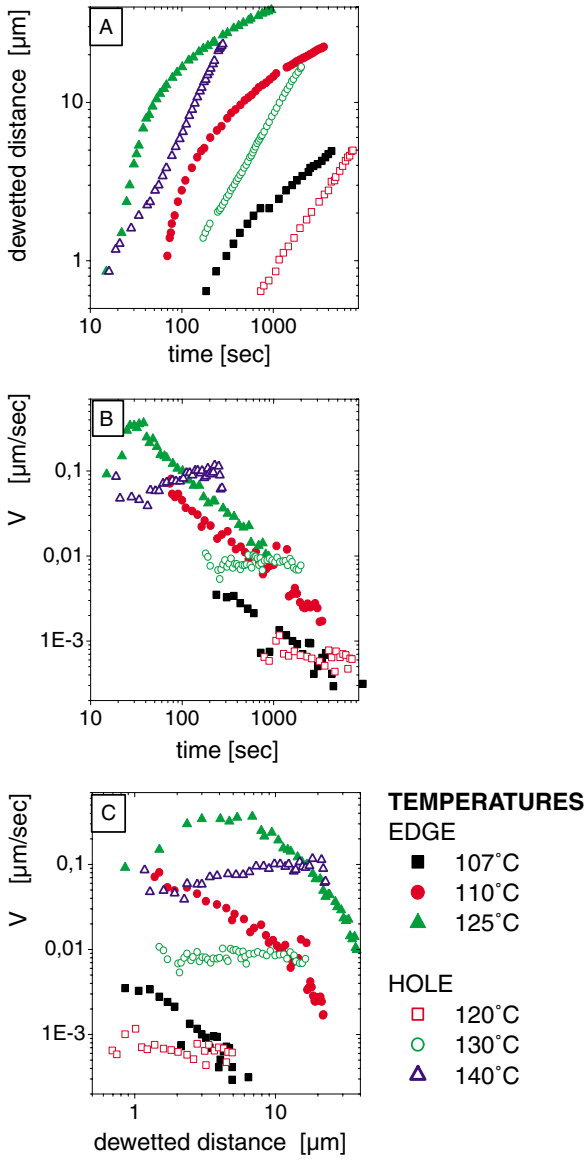

Fig. 5. Dewetting at different temperatures of a 100 nm thick PS125k film on a grafted PDMS78k layer of 17 nm, from the edge (full symbols) and opening of a hole (open symbols). A) Dewetted distance as a function of elapsed time on logarithmic scales. B) and C) for the same data, dewetting velocity as a function of time and dewetted distance, respectively, on logarithmic scales. Please note that the temperatures are *not* the same for dewetting from the edge and opening of a hole.

decreased. This intermediate period where the hole opening velocity is constant represents the most important difference between the results obtained in the two dewetting geometries. At present it is not yet clear how and why initially the dewetting geometry has such a measurable effect on the dewetting process. It is also remarkable that after these initial stages the results from both geometries tend to converge to yield the same behavior.

The data for Figure 4 were taken at 110 °C, *i.e.* only a few degrees above the glass transition. The comparison of these results with the ones shown in Figures 1 and 2 indicates that in the temperature range between 110 °C and 140 °C, we observe qualitatively the same behavior, only the dewetting velocity at the onset of dewetting differs. In the regime where the velocity of the opening of holes is almost constant (within the temperature range between between 107 °C and 140 °C, see Fig. 5), we find an almost exponential temperature dependence of this velocity: $V \sim \exp(aT)$, with a being a constant. In contrast, for dewetting from the edge, such a relation is not obvious as there is no time interval where the velocity is constant. For the very early stages of small dewetted distances (*e.g.*, 2 microns), however, it is possible to compare the dewetting velocities obtained at different temperatures. Such a comparison yields a similar exponential temperature dependence of the dewetting velocity, but now V is also a function of the dewetted distance. On the other hand, our data indicate that, within experimental error, the same dewetting velocity for retraction from the edge is obtained for all curves at late stages, independent of temperature. This observation is consistent with the results for the higher molecular weight PS shown in Figure 1 for the opening of holes. There, after the initial period of constant velocity, all holes open at about the same velocity, again independent of temperature. We believe that this intriguing influence of temperature on dewetting represents the most challenging aspect to understand.

4 Conclusions

Although several additional measurements (*e.g.*, the influence of the properties of the PDMS coating, dependence on PS layer thickness) are necessary to complete this study, several surprising observations are already evident. Our results show that for highly viscoelastic PS films it is initially more difficult to open a hole than to retract the film from the edge (a straight line) of the sample. Besides quantitative differences in the initial velocity, also qualitative differences in the time dependence of this velocity exist between these two geometries. Only for the opening of holes, a distinct regime of constant velocity is found. At present, it is not yet clear what causes the different behaviors in the two geometries. However, a comparison with the results obtained for liquid PDMS films [18] strongly indicates that the high elastic modulus (close to the glass transition) is the most relevant parameter. As shown previously [12], the driving capillary forces cause a plastic deformation of the sample (the polymer is not flowing like a Newtonian liquid). This conclusion is also supported by the similitude in the behavior (see Fig. 2) of the two studied PS of largely different molecular weight (PS125k *vs.* PS3900k), in particular during late stages where a fully developed rim has been formed. Maybe the most remarkable result we have presented is the rapid decrease in dewetting velocity with time, reaching almost a standstill at dewetted distances which are in the range of 10 micrometers. This slowing-down is related to an increase in the dewetted distance with the logarithm of time. Such a peculiar time dependence, and

all the other unusual dewetting behaviors (*e.g.*, the influence of geometry), still need an explanation. We hope that our experimental results presented here will again initiate corresponding theoretical works.

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