The Elastic Mechanical Response of Supported Thin Polymer Films

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Supporting Information:

In a typical nanoindentation experiment, the interaction force between the indenter and sample surface is recorded as function of force distance, quantified in terms of a force-distance (FD) curve (see Figure 1 in the main manuscript). The effective modulus, *E*, is estimated based on a contact mechanics model; typical modules include the Hertz,[1] Oliver-Pharr (OP),[2-3] Johnson-Kendall-Roberts (JKR),[4] and Derjaguin-Muller-Toporov (DMT) models.[5] The Hertz, JKR, and DMT models are valid under conditions of elastic deformation. While the Hertz model neglects effects due to the adhesion between the tip and sample surface, the other two models account for the effects of adhesion.[6] On the other hand, the OP model, which estimates *E* from the initial slope of a retraction curve,[2-3] is appropriate for conditions of elastic-plastic deformation. The OP model has been reported to overestimate the modulus possibly due to plastic deformation and pile-up in the vicinity of the indentation center and to the viscoelasticity of polymers.[7-8]

In a recent publication Dokukin and Sokolov, discussed the utility of using different models to extract the elastic modulus E from a force-Distance, FD, curve, measured using an atomic force microscope (AFM)   They employed Hertz, OP, JKR, and DMT models to fit same set of FD curves that were measured using a sharp tip (radius, $R \sim 22$ nm) and a hemispherical tip ($R > 810$ nm), . For FD curves obtained with the sharp tip, regardless of which model was used for the analysis, an enhancement in E was observed for small indentation depths. In contrast, the enhancement of E disappeared when FD curves were obtained using hemispherical tips and employing the JKR and DMT models, which accounted for the effects of adhesion between the tip and the sample surface.. Their concluded that the enhanced moduli at small indentation depths may originate from the nonlinearity of stress-strain relation (with the use of a sharp tip) and when the adhesion between the tip and sample surface is neglected from the analysis.

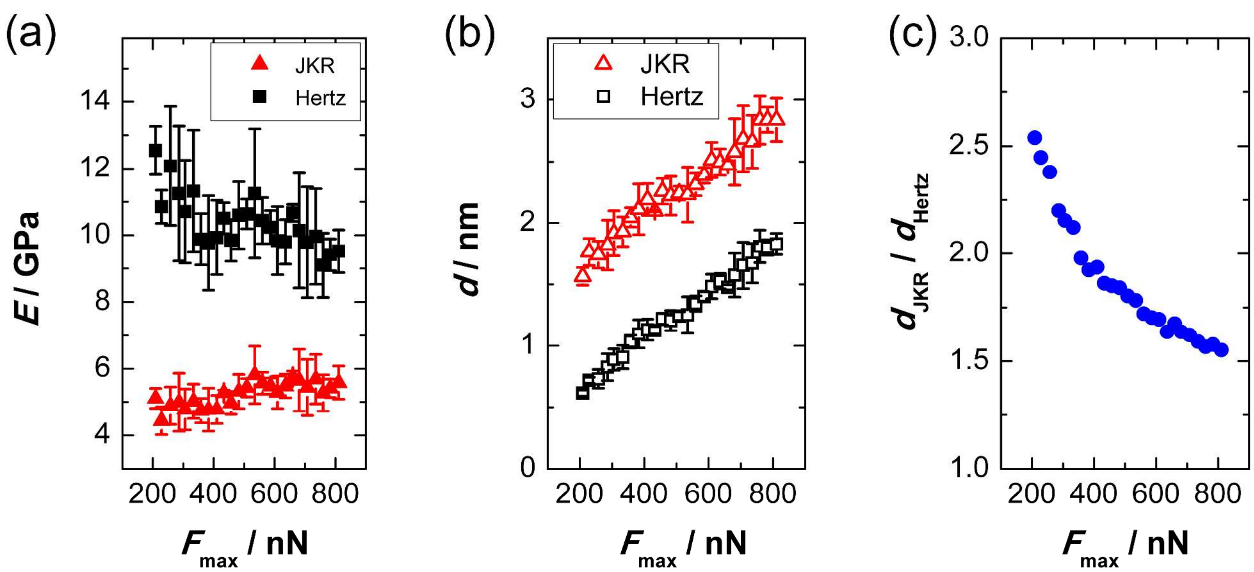

Figure S1. (a) Same set of force-distance curves was fitted with the Hertz model (filled squares) and JKR model (filled triangles) and the effective moduli, E, are plotted as a function of maximum force, F_{max}. Each data point is an average of 3 nanoindentation measurements. (b) The corresponding indentation depths, d, from data shown in part (a) are plotted with open symbols as a function of F_{max}. Each data point is an average of 3 nanoindentation measurements. (c) The relative underestimation of d (ratio of d estimated by the JKR and Hertz models) is shown as a function of F_{max}.

AFM nanoindentation measurements were performed on a ~1 μm thick polystyrene film, supported by oxidized silicon substrate, using different maximum forces, from 200 nN to 800 nN. The Hertz and JKR models were used to extract E from a same set of FD curves and results are shown in Figure S1a. When the Hertz model s, which neglects the effects of adhesion between the tip and film surface,[6] was used to fit the FD curve the estimated E increased with decreasing F_{max} or indentation depth, d. In contrast, only a slight increment of the moduli was observed with increasing F_{max} when the analysis was performed using the JKR model, which accounts for the effects of dhesion. This slight increase in E with increasing F_{max} can be attributed to effects associated with the underlying stiff substrate; the stress field created under indentation propagates further into the film with increasing F_{max}. The enhancement in E is observed due to increasing interactions between the stress field and underlying substrate (the "substrate effect").[9] Indentation depths estimated using the JKR model (d_{JKR}) and the Hertz model (d_{Hertz}) are plotted as a function of F_{max} in Figure S1b and it is shown that the Hertz model underestimates indentation depths compared to those estimated by the JKR model. The relative underestimation of indentation depth (d_{JKR}/ d_{Hertz}), plotted in Figure S1c, reveals that the relative underestimation is larger for lower values of F_{max}; the extent of the underestimation decreases with increasing F_{max}. It is important to point out that the dependence of d_{JKR}/ d_{Hertz} on F_{max} exhibits a trend similar to the enhancement of the moduli shown in Figure S1a. This suggests that the increasing E with decreasing F_{max} (Figure S1a) originates from an underestimation of the indentation depth with decreasing F_{max} (Figure S1c). Our observations are in agreement with those of Dokukin and Sokolov.[10] Therefore we used the JKR model the analysis of the indentation data in our study.

References

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