P. G. de Gennes' contributions to understanding adhesion

~ 20 papers between 1982 and 1996

Situation before de Gennes' contributions

Most work in adhesion was in the following areas:

- Polymer and network synthesis (synthetic chemistry)
- Wetting of the adhesive on the substrate
- Mechanical testing - particularly fracture mechanics of interfaces (mechanical engineering)
- Little polymer physics except for the work of Alan Gent

De Gennes' main contributions

- Chain interpenetration and welding
- Adhesion between weakly immiscible polymers
- Viscoelastic fracture
- Brush interpenetration and chain pullout from a crosslinked elastomer

Interpenetration and Welding
- only concerned with short times

Influenced by the experiments of Kausch's group
which showed the toughness $G_c \sim t^{1/2}$

1) What is the initial situation, where are the chain ends?
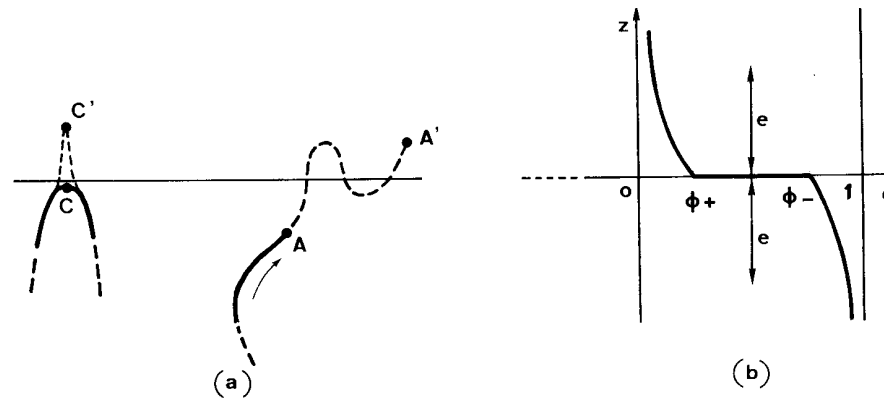2) Interdiffusion for times less than a tube renewal time.

Fig. 2

3) What is the relation between chain interpenetration and interface toughness?

By making plausible assumptions he derived the experimentally observed power law but

1) The experiments were done with samples with a broad molecular weight distribution
2) The relation between interpenetration and toughness was not known at that time.

In spite of more recent work, I consider that the problem is still unsolved.

Adhesion between weakly immiscible polymers - effect of χ and hence interface width

He considered the interface to be coupled by arcs of polymer chain of length $> N_e$, shorter arcs were considered to be ineffective.
The arc density was controlled by χ.

He assumed a chain pullout type of relation between G_c and the areal density of effective arcs.
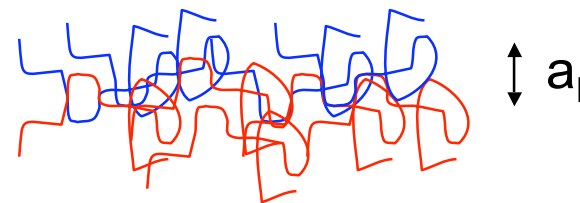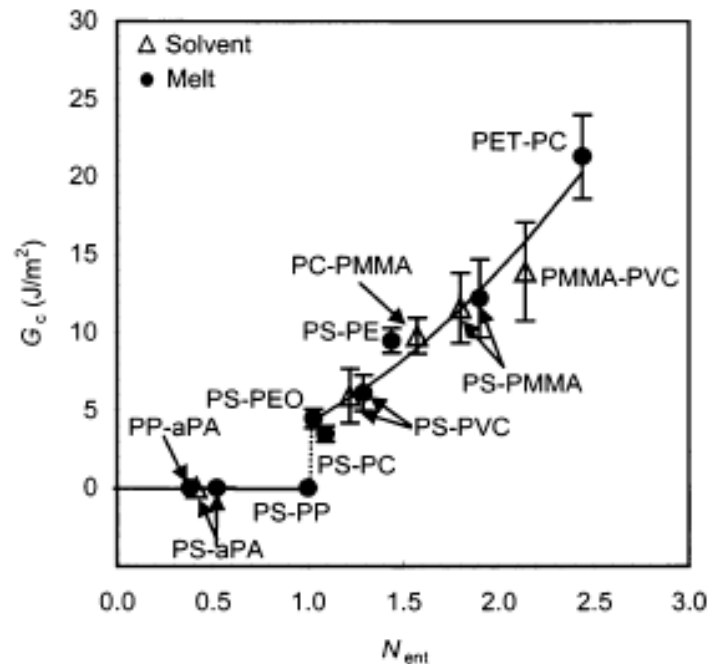
$$G_c = G_o N_e^{1/2} (\chi N_e)^{-1/2} \exp(-\chi N_e)$$

More recent work

The amount of entanglement across an interface is expected to be controlled by:

$$a_r = N_{ent} = a_I / L_e$$

where the interface width is a_I and the distance between entanglements is L_e

Figure 5. Adhesion data obtained using the DCB test. Solvent (△) and melt (●) laminated samples were prepared using the indicated polymer pairs. Error bars represent the standard deviation of 8−10 samples.

Evidence from a range of polymer pairs

P. J. Cole,† R. F. Cook, and C. W. Macosko* *Macromolecules* **2003,** *36,* 2808-2815

Calculation of the number of chains crossing the interface and relation between across-interface entangled chains and G_c
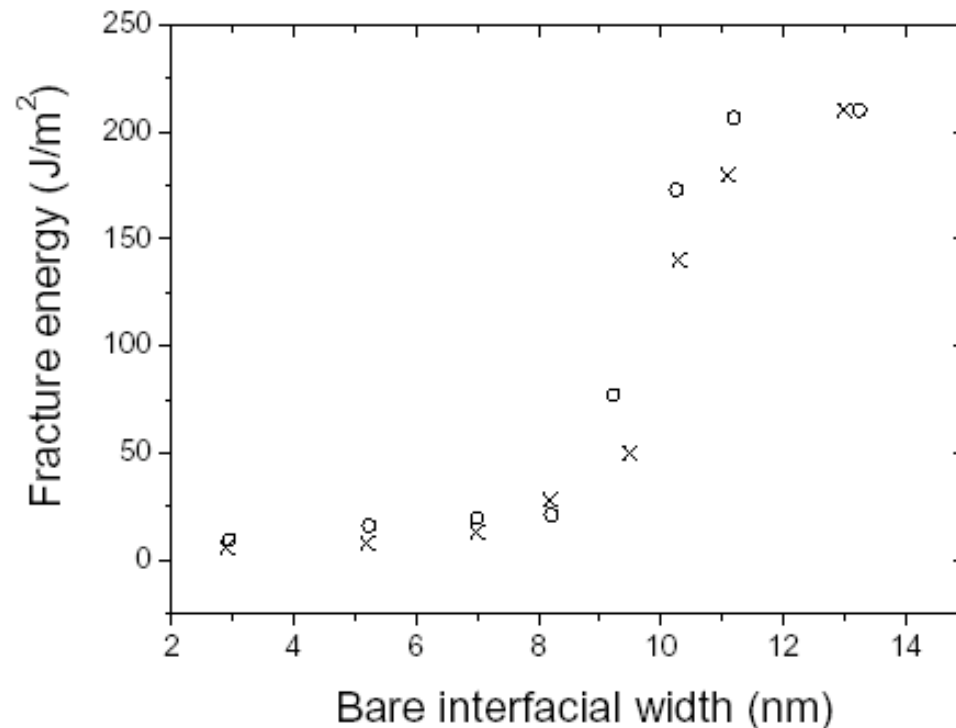
Used a self consistent mean field theory based way of calculating the number of chains that cross an interface and my craze fracture model.

L. Silvestri, H. R. Brown, S. Carrà, S. Carrà, *Journal of Chemical Physics* **119**, 8140-9 (2003)

Fracture energy as a function of the bare interfacial width for PMMA/P(S-r-MMA), calculated from the model (circles). Crosses represent my experimental data.

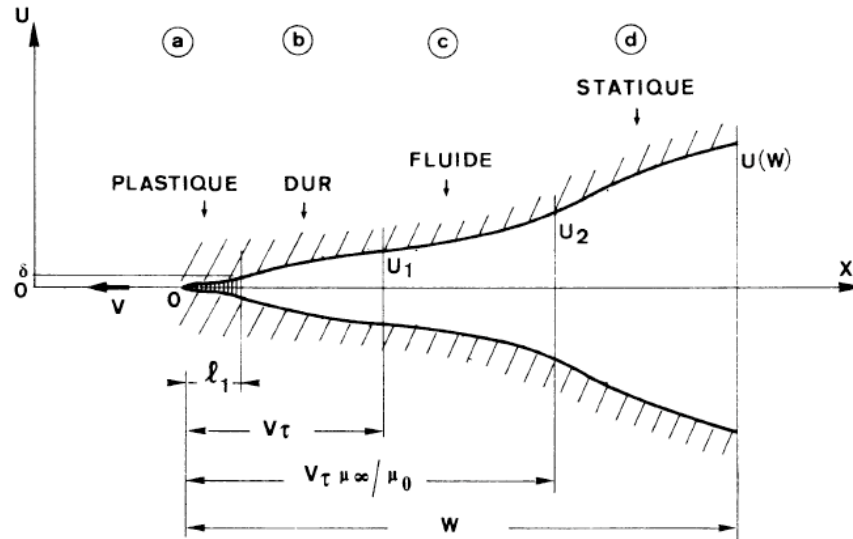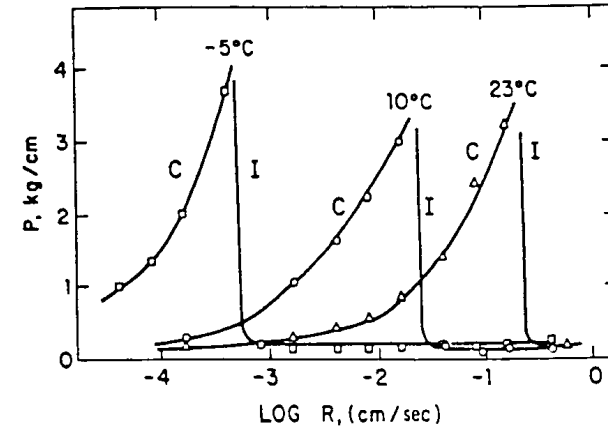# De Gennes' viscoelastic trumpet

Fig. 1. — La « trompette » : fracture dans le régime V > l_1/τ.
Les deux régions dissipatives sont (a) et (c).

Fig. 1. — The "trumpet": fracture shape in the regime V > l_1/τ.
There are two regions of strong dissipation: (a) and (c).

Figure 1. Peel force P versus peel rate R for an un-cross-linked butadiene–styrene rubber adhering to a PET polyester film after ref 3. The symbols C and I denote cohesive failure and interfacial failure, respectively.

Aim was to explain the results of Gent and Petrich.
Fluid (dissipative) region exists between radii U_1 and U_2 round the crack and hence increases in size with increasing crack speed.
Dissipation hence increases with crack speed but there is a maximum dissipation controlled by sample size.

Fracture d'un adhésif faiblement réticulé, C.R. Acad Sci. 307, 1949 – 1953 (1988)

Pullout of connector molecules from an elastomer
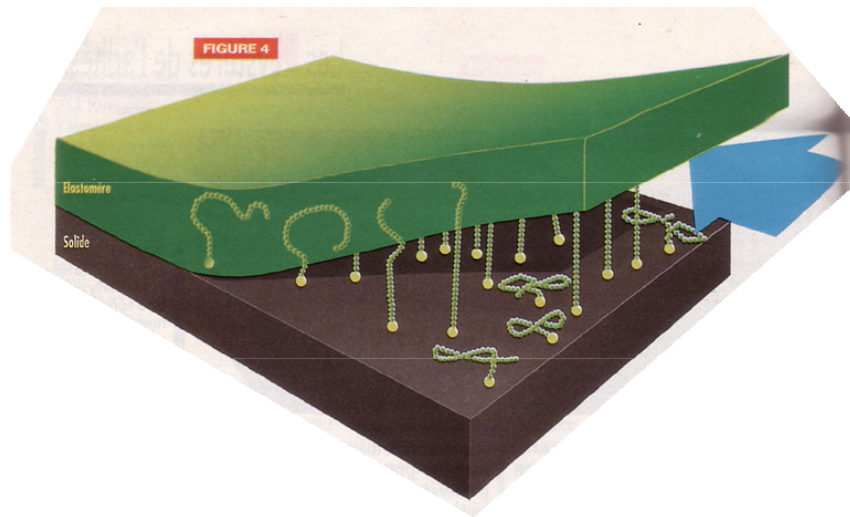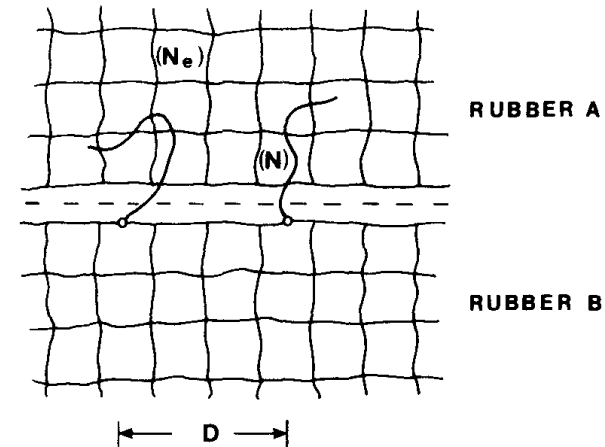
Figure 1. A model for a weak rubber (A)/rubber (B) junction. The two parts are connected by long A polymer chains (adhesion promoters) grafted to the network B and entering freely in the A block.

The aim of the work was to calculate the energy dissipated in pulling the connector molecules from the elastomer (RUBBER A)
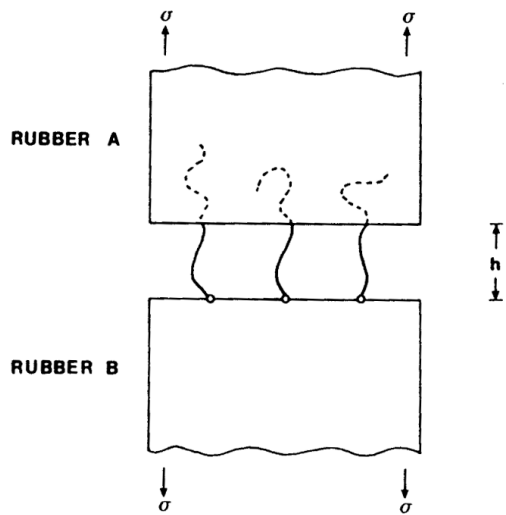
E. Raphael and P. G. de Gennes, Rubber – rubber adhesion with connector molecules, J. Phys. Chem. 96, 4002 – 4007, (1992)

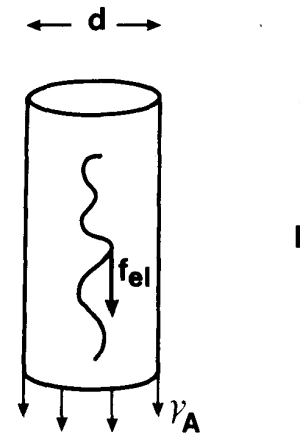Figure 2. The two rubber blocks submitted to a uniform tensile stress σ.

Figure 3. A connector bridging the air gap (of thickness h) between the two blocks A and B. We describe the bridge as a "pillar" of diameter d and height h. The pulling force necessary to maintain the pillar is a combination of a capillary force $f_c \sim \gamma_A \pi d$ and an elastic force f_{el}.

The crucial realization of this work was that, to pull a chain out, it has to be highly stretched across the void and so in a highly energetic state. This energy is lost when the chain finally detaches from rubber A

The connector molecules contribute to the zero velocity toughness, G_0.

$$G_0 = W + \gamma \Sigma N$$

W is the thermodynamic work of adhesion, N the degree of polymerization of the connectors of areal density Σ and surface energy γ.

Chain pullout in polyisoprene

Go

G (J/m²) vs Σ (chains/nm²)

- ■ N_PI=2205
- ○ N_PI=882
- ▲ N_PI=588
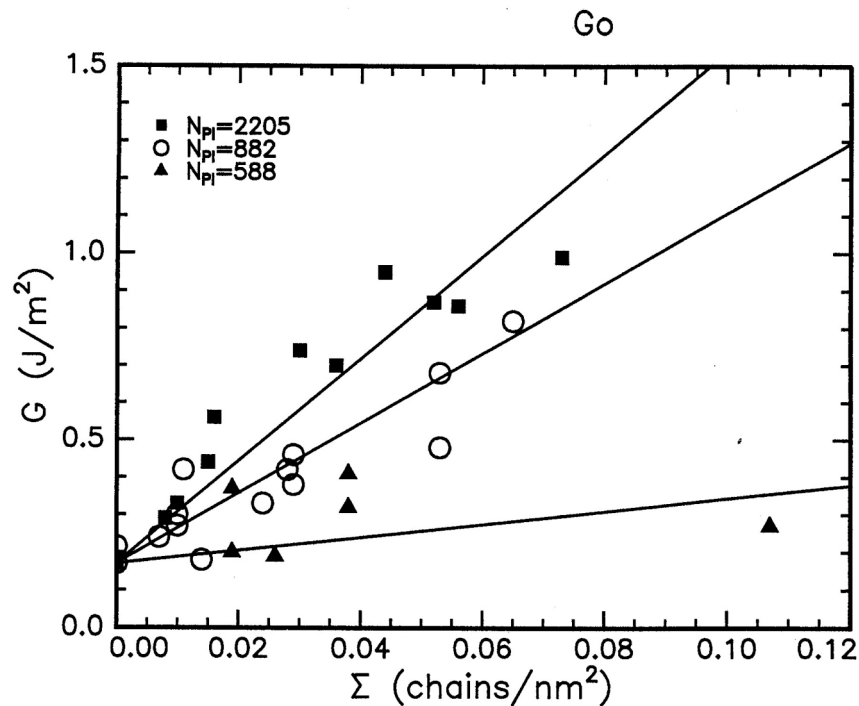
Isoprene tethered chain from isoprene network – G_o varies linearly with Σ?

Chain pullout from Elastomers

Polyisoprene lens on tethered polyisoprene – at low coverage experiments are consistent with Raphael and de Gennes model but not definitive.

Questions

What is the driving force for tethered chains to enter the network? What happens at high coverage?
How long does it take for the tethered chains to fully enter the elastomer gel? Perhaps months.
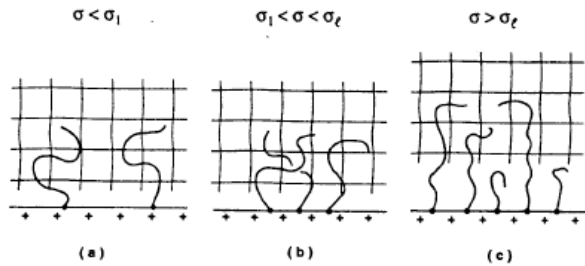
Partial interdigitation

Figure 4. Three regimes for a brush exposed to a rubber: (a) separate mushrooms; (b) overlapping mushrooms; (c) partial interdigitation.
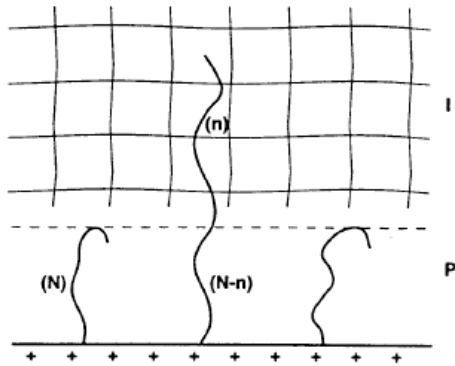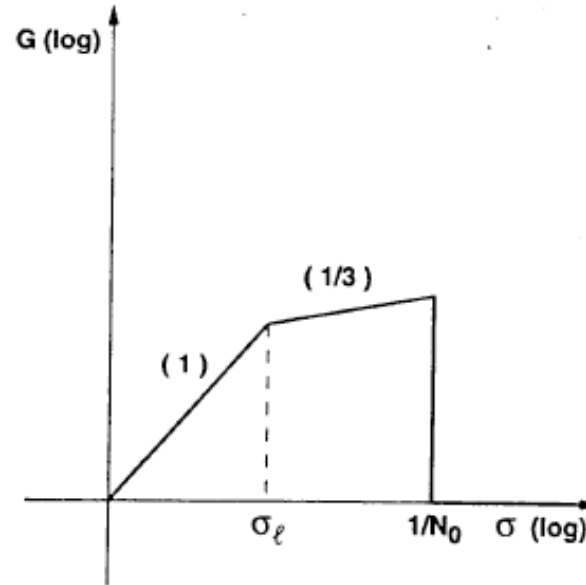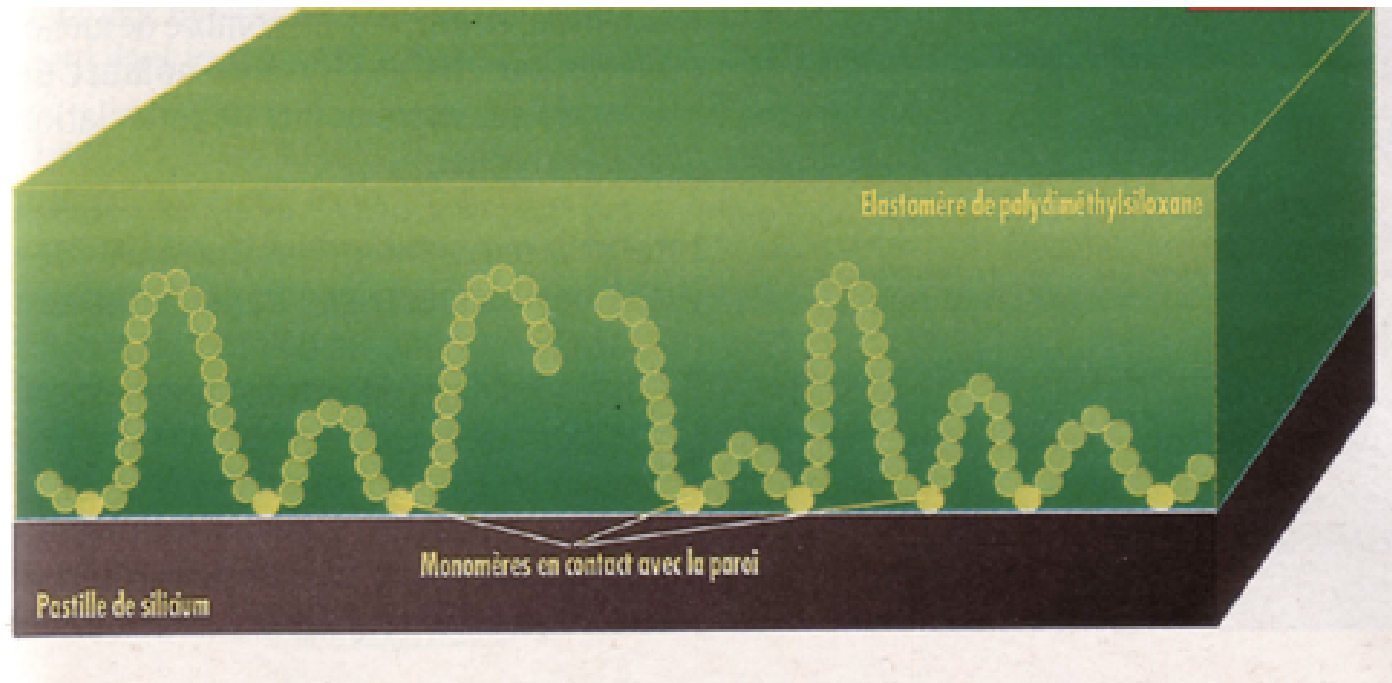
Figure 5. Partial interdigitation between a grafted brush and a rubber: (I) interdigitated region; (P) passive layer. A fraction f of the chains penetrates into I.

De Gennes and co-workers wrote a number of papers on partial interdigitation and also considered the penetration and pullout of a pseudo brush (see next slide).

Chain Pullout from a pseudobrush

More recent models of chain penetration

If the tethered chain enters the network its free
energy per chain of the form:

Brush thickness   Grafting density

$$\frac{F}{kT} \simeq \frac{L^2}{a^2 N} + \frac{a^2 N}{L^2} + \frac{\sigma N^2 a}{PL}$$

Repeat units in brush chains   Repeat units in network

The elastic energy of the network causes the
tethered chain to stretch, but why does it enter at all?

Brush-network interfacial energy

If the brush does not enter the network it forms a dense layer with an interface to the network of width λ equal to the network spacing. Hence there is a interfacial energy of the form $a/\sigma\lambda$ added to the free energy per chain.

When the chain density σ is small this can be a large term so removal of the interface by interdigitation is favored.

Full penetration when $$\sigma < \sigma^* \simeq P^{\frac{1}{10}}/N^{\frac{3}{5}}$$

T. Vilmin, C. Tardivat, L. Leger, H. R. Brown and E. Raphael, *Europhys. Lett.* **68** (4) 543-549 (2004)

What happens when $\sigma > \sigma^*$?

Initially the energies of the two states are similar so assume fluctuations and take a thermodynamic average.
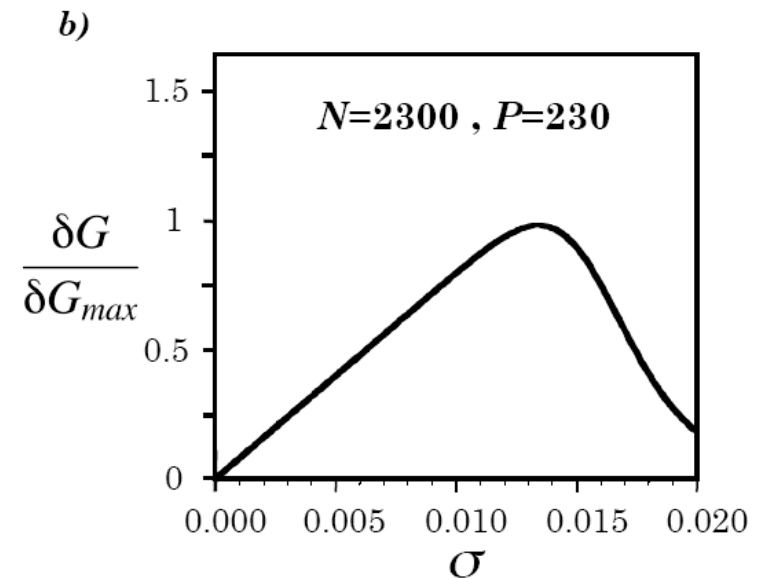
Experiments

PDMS network on a layer of long PDMS chains
tethered to a silicone wafer. Also dense short chains
to protect the network from the silicon oxide.

Adhesion measured by JKR (elastomer lens on flat).
Left in contact for 15 hours.
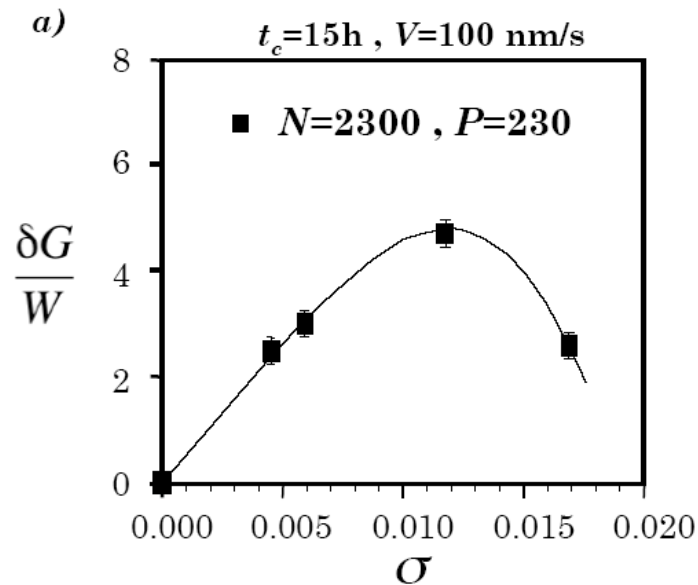
Experiment

Theory

Summary

PGG worked in a number of different areas in polymer adhesion. His main contribution has been to show that a polymer physics approach is very useful in connecting between the chemistry and the mechanics.