

# Grafted polymers are miniaturized pressure tools

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**Abstract.** Development of techniques to characterize and manipulate matter at the mesoscopic level ( $1-10^3$  nm) has been the cornerstone of recent technological and scientific progress in biology, physics and chemistry. Many of the techniques rely on the possibility of applying well defined forces at the relevant lengths scales: revealing the structure of colloidal interactions with a surface force apparatus (SFA) (Israelachvili J., *Intermolecular and Surface Forces*, Academic Press, London, 1992); imaging biologic and other soft materials with an atomic force microscope (AFM) (Binnig G., Quate C.F., Gerber C., *Phys. Rev. Lett.* 56 (1986) 930); manipulating DNA, vesicles or emulsions with optical tweezers (Ashkin A., Dziedzic J., Bjorkholm J.M., Chu S., *Opt. Lett.* 11 (1986) 288)... We argue here that grafted polymers rightfully belong to the family of mesoscopic force tools, and predict the forces that these tools are expected to exert in a number of experimental situations. © 2000 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

**grafted polymers / pressure tools / surfaces / membranes**

## *Polymères greffés : des outils de pression miniaturisés*

**Résumé.** Le développement de techniques permettant de caractériser et de manipuler des objets mésoscopiques ( $1-10^3$  nm) a été au coeur des progrès scientifiques et technologiques récents en biologie, en physique et en chimie. Ces techniques requièrent, pour la plupart, la possibilité d'exercer des forces bien définies aux échelles adaptées. On révèle ainsi la structure des interactions colloïdales avec une machine de force (Israelachvili J., *Intermolecular and Surface Forces*, Academic Press, London, 1992); on sonde la matière biologique et autres matériaux mous avec des microscopes à force atomique (Binnig G., Quate C.F., Gerber C., *Phys. Rev. Lett.* 56 (1986) 930); on manipule l'ADN, les vésicules et les émulsions avec des pinces optiques (Ashkin A., Dziedzic J., Bjorkholm J.M., Chu S., *Opt. Lett.* 11 (1986) 288)... Nous proposons dans cette note de considérer les polymères greffés comme appartenant à cette classe d'outils et calculons les forces auxquelles on peut s'attendre dans plusieurs situations expérimentales. © 2000 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

**polymères greffés / outils de pression / surfaces / membranes**

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## *Version française abrégée*

Les polymères sont des longs enchaînements de monomères, leurs unités de base. Un polymère flexible en solution a une taille typique de un à cinquante nanomètres. Quand une chaîne polymère approche une paroi répulsive, certaines des configurations permises en volume ne sont plus réalisables. Cette réduction d'entropie engendre une pression non-homogène sur la paroi, dans une région comparable à la taille du polymère. Nous calculons ce champ de pression pour plusieurs géométries de fixation du polymère.

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Note présentée par Pierre-Gilles DE GENNES.

Pour un polymère greffé par un bout, la pression dans le voisinage du point de greffage varie comme  $p(r) \sim K_B T r^{-3}$ , puis s'amortit exponentiellement pour des distances supérieures à la dimension du polymère ( $r$  est la distance au point de greffage, mesurée sur le plan). Quand le bout libre de la chaîne est maintenu à une distance  $z$  de la paroi, la portée du champ de pression est réduite, mais la structure d'échelle proche du point de greffage est maintenue. En pratique la manipulation du bout libre peut être effectuée en chargeant quelques monomères proches de cette extrémité de la chaîne, puis en contrôlant la force ionique de la solution.

Dans les deux configurations précédentes la pression varie très rapidement autour de son maximum, au point de greffage. Des variations moins brusques peuvent être obtenues dans une géométrie de confinement. Si l'on attache le polymère sur une paroi (la surface mica d'une machine de force, la pointe d'un microscope à force atomique) que l'on approche à une distance  $D$  d'une surface répulsive lui faisant face, la pression maximale, au centre du champ de pression, est de l'ordre de  $p(r=0) \sim K_B T / D^3$ , puis varie doucement sur une distance comparable à la taille du polymère.

La température peut aussi être utilisée comme paramètre de contrôle de la pression, surtout lorsque l'on induit une transition d'adsorption à la paroi, ce qui peut annuler le champ de pression.

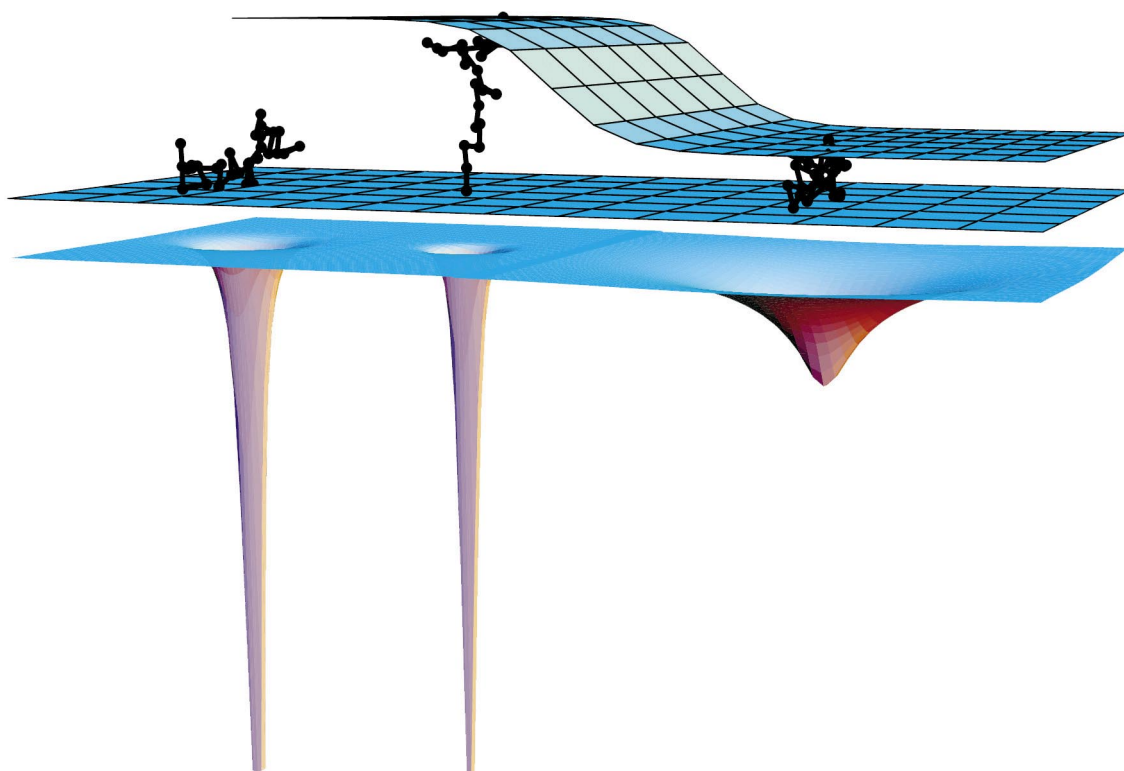
A polymer is a long chain of connected monomers, its building molecular units. A flexible polymer in solution has typical dimensions in the range 1–50 nm. When a polymer chain is brought to the neighbourhood of a repulsive, impenetrable wall, the number of conformations available to the chain is reduced [1]. Such a reduction of conformational entropy creates a nonhomogeneous pressure field acting on the wall in a region comparable to the polymer size. As we will now show, the pressure field can be controlled by choosing how the chain approaches the surface but also by tuning the chain size and architecture.

A frequent experimental situation involves end-grafted polymers, linear chains that are bound to the surface by their extremities. In the case of a gaussian end-grafted chain (see the *figure*), a particular simple model where the monomers are excluded from the wall but do not mutually interact, the pressure  $p$  can be obtained by calculating [2] the virtual work of an arbitrary deformation of the grafting surface. The pressure has the following radially symmetric form:

$$p(r) = \frac{1}{2\pi} \frac{K_B T}{(r^2 + a^2)^{3/2}} \left( 1 + \frac{r^2 + a^2}{2R^2} \right) \exp \left\{ -\frac{r^2 + a^2}{4R^2} \right\} \quad (1)$$

where  $r$  is the in-plane distance from the grafting point,  $K_B$  is the Boltzmann constant,  $T$  is the absolute temperature and  $R^2 = Na^2/6$  is the typical size of a gaussian polymer with  $N$  monomers of size  $a$ . Close to the grafting point ( $r = 0$ ) the pressure can be as high as  $10^7$  Pa for  $a = 0.3$  nm at room temperature  $T = 25^\circ\text{C}$ . The pressure strength sharply decays from the centre as  $p(r) \sim K_B T r^{-3}$ , and vanishes exponentially for distances larger than the polymer size ( $r \gg R$ ). The  $r^{-3}$  dependence is the natural scaling form for the pressure, we also expect it to hold for chains with excluded volume. The total force  $f$  exerted by the polymer onto the surface,  $f = \int_0^\infty 2\pi r p(r) dr \simeq K_B T / a$  is of order of a few pN, independently of polymer size. The grafted monomer exerts a point like force  $-f$  that ensures mechanical equilibrium. By pulling on the free end of the polymer one can modify the pressure applied to the wall. If the free end is hold at a distance from the wall  $z = \alpha R$  (see the *figure*), the size of the region where the pressure is applied is reduced from  $R$  to  $R/\alpha$ , but the pressure intensity close to the grafting point has the same sharp form:

$$p(r) \approx \frac{1}{2\pi} \frac{K_B T}{(r^2 + a^2)^{3/2}} \exp \left\{ -\frac{r^2 + a^2 + 2zr}{4R^2} \right\} \quad (2)$$



**Figure.** The pressure applied by grafted polymers to a repulsive surface in three different situations. The pressure applied to the bottom mesh surface is shown in arbitrary units below each configuration. The grafting points exerts a point like force  $-f$  (not shown), that pulls the surface, enforcing mechanical equilibrium  $f = \int_0^\infty 2\pi r p(r) dr \approx K_B T/a$ . From left to right: polymer grafted by one end to the surface where the pressure is measured; same situation but with the second end pulled away from the surface; polymer grafted by one end to an opposing surface. Note that only snapshots of the polymers are shown, their average densities are also radially symmetric.

**Figure.** La pression exercée par des polymères greffés sur une surface répulsive dans trois situations différentes. La pression exercée sur la surface inférieure est montrée dans des unités arbitraires mais comparables, sous chaque configuration. Les points de greffage appliquent aussi une force ponctuelle  $-f$  qui tire sur la surface et garantit l'équilibre mécanique. De gauche à droite : polymère greffé par un seul bout sur la surface où la pression est mesurée ; la même situation mais avec le deuxième bout maintenu loin de la surface ; polymère greffé par un bout sur une surface opposée. Seules des images instantanées des configurations sont montrées, leur configurations moyennes étant bien entendu radialement symétriques.

At a distance  $r = 1$  nm from the grafting point, a polymer with one hundred monomers and monomer size  $a = 0.3$  nm ( $R = 2.2$  nm) will exert a pressure of roughly six atmospheres:  $p \approx 6 \cdot 10^5$  Pa. Pulling the end of the polymer away from the surface by twice the radius of gyration of the chain to a distance  $z = 4.4$  nm will reduce the pressure to one atmosphere,  $p \approx 1 \cdot 10^5$  Pa. In practice, pulling the end away from the surface can be achieved by charging some of the monomers close to the free-end of the chain. Even if the grafting surface is not charged the monomers will be repelled by their image charges. For instance, at the interface between oil and water, in absence of added electrolyte, the forces between  $Z$  charges at the free end of the chain and their images will pull the chain end to a distance  $d_Z = R \times (Z/Z^*)^{2/3}$ ,  $Z^* = (2R/\ell_B)^{1/2}$  being the minimum amount of charges needed to pull significantly the free end from its equilibrium position.  $\ell_B = e^2/(4\pi\epsilon_r K_B T)$  is the Bjerrum length, a characteristic electrostatic distance,  $\ell_B = 0.7$  nm in water

where  $\epsilon_r \approx 80$ . For the chain considered above,  $Z^* \approx 2.5$ , and seven charges are enough to bring the chain end to a distance  $d_Z = 2R$ . Interestingly, in this configuration, an increase of the ionic strength of the solvent will also increase the polymer pressure on the wall. Indeed, a reduction of the electrostatic repulsion due to electrolyte screening will bring the free-end closer to the wall, increasing the pressure according to equation (2).

In the two chain configurations considered above the forces vary sharply from the maximum at the grafting point. Shallower forces can be obtained in other configurations. For instance, if a polymer is grafted to a solid surface (a SFA mica surface or an AFM tip) and then brought into a distance  $D$  of an opposing repulsive wall, the structure of the pressure field is rather different (see the *figure*). At the centre the pressure maximum depends on the separation distance as:

$$p(r = 0) \sim \frac{K_B T}{D^3} \quad (3)$$

A separation  $D = 3$  nm leads to a central pressure of  $10^4$  Pa, a factor thousand below the precedent configuration. Nevertheless, due to a smooth decay of the pressure over a distance  $R$ , the total applied force  $f = (K_B T/D^3)8\pi R^2$  can be large: a chain with  $R = 30$  nm confined in a 3 nm gap will apply a total force of 0.5 nN.

Tuning the temperature allows also to control the forces exerted by the polymer, mostly by varying the wall–polymer interactions. Indeed the polymer pressure is rather independent of solvent quality, as far as the chain does not collapse, below its  $\theta$  point. The expansion of the polymer coil under the effect of excluded volume interactions do translate into an increase of the pressure range, but we expect that the pressure intensity close to the grafted point will always scale as  $p(r) \sim K_B T r^{-3}$ . However, any change in the wall potential that induces a wall attraction of the polymer will drastically reduce the pressure when the temperature crosses the adsorption threshold.

Polymers can be grafted or brought close to a number of soft interfaces: surfactant or phospholipid bilayers in cells, in vesicles and in other membrane solutions; air–liquid or liquid–liquid interfaces in Langmuir monolayers or in microemulsions [3]. . . Under the polymer pressure, these interfaces bend into characteristic average shapes that depend on the restoring surface forces counteracting the pressure: bending rigidity, surface tension, electrostatics, . . . The shape of soft interfaces can therefore be manipulated by using these polymer tools, and conversely, the distortion shape can be used as a sensor for gauging the applied pressure. A particularly suitable experimental configuration to study these effects would be to attach polymers to giant vesicles [3], and observe the induced deformation under a microscope. Moreover, polymers are versatile molecules that can be tailored in many sizes and architectures, well beyond the simple examples discussed here. Such versatility can be translated into a wide range of available pressure forms and strengths, further enhancing the possibility of designing ‘à la carte’ mesoscopic force tools, suitable for each given application.

## References

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