



ADSORPTION OF THE POLYMER ON A CLAY MATRIX : THEORETICAL STUDY

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INTRODUCTION



- The adsorption of polymers has been the subject of several theoretical studies with the aim of understanding the phenomenon and developing new theoretical approaches. Several models have been proposed by Kuhn, Flory, Edwards, Sulberberg and others, but most of them have shown their limits and give results very far from experimental reality.
- The scaling law proposed by De Gennes makes it possible to include interactions between monomers and the effects of the solvent. This theory has succeeded in deriving equations which show good agreement with experience.
- The very important applications of adsorption on interfaces, more precisely in the stabilization and destabilization of colloidal suspensions, have motivated the search for more realistic models.

GOAL OF THE STUDY

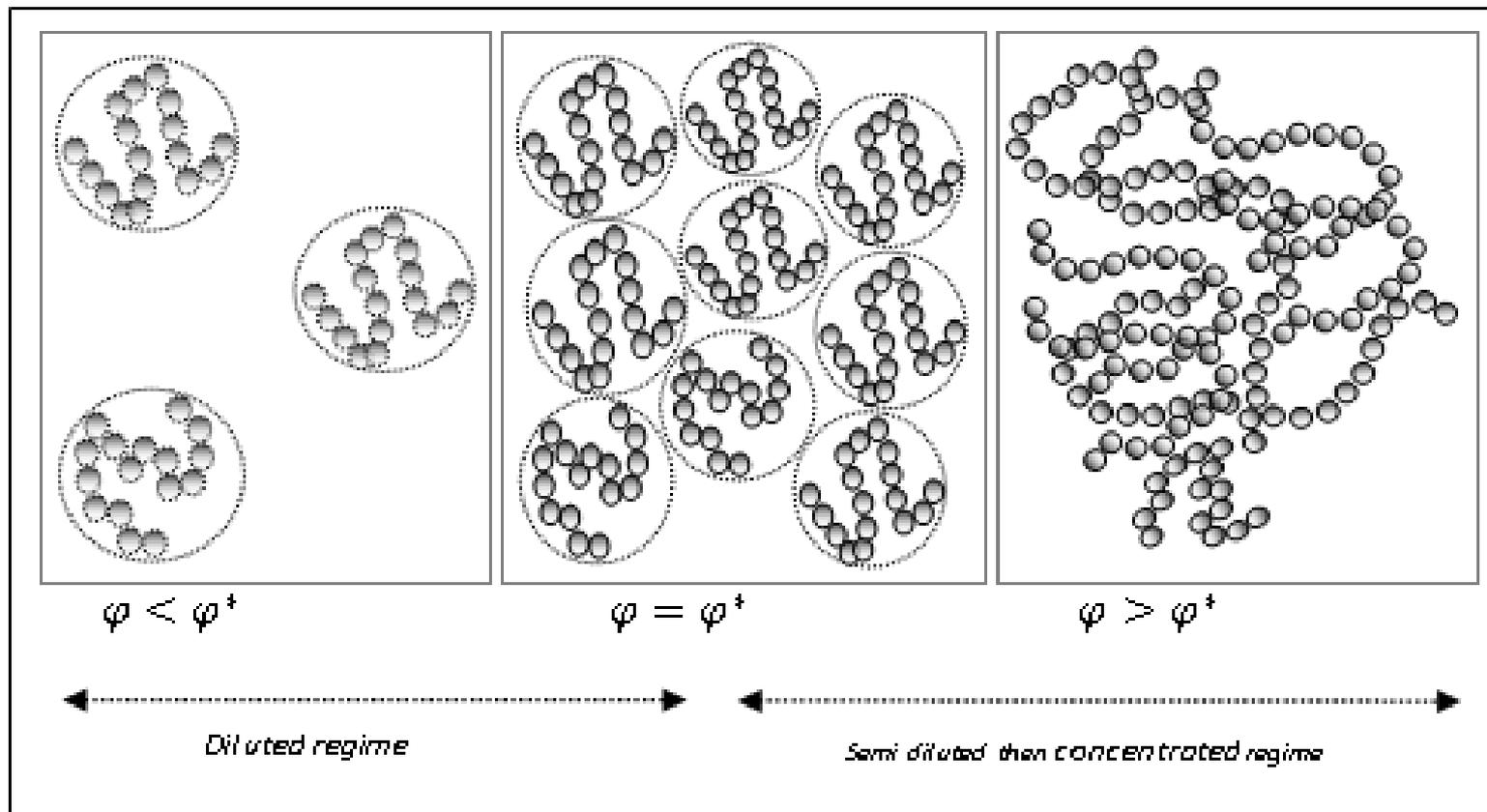


- Contribute to understanding the adsorption phenomenon of neutral and flexible macromolecules on an impenetrable, flat and attractive surface in the case of a good solvent.
- Evaluation of the coverage rate Γ of the surface as a function of the volume fraction of monomer φ in the case of the bulk diluted regime for which the surface traverse three regimes (diluted, bidimensional semi-diluted, and plateau).
- Variation of the volume fraction along the axis perpendicular to the surface (z). The three regions (proximal, central and distal) will be discussed.

DILUTED BULK REGIME



- When the volume fraction of monomer is less than a threshold fraction φ^* the solution is in the diluted regime, the polymer chains are independent and can be considered as single isolated chains.

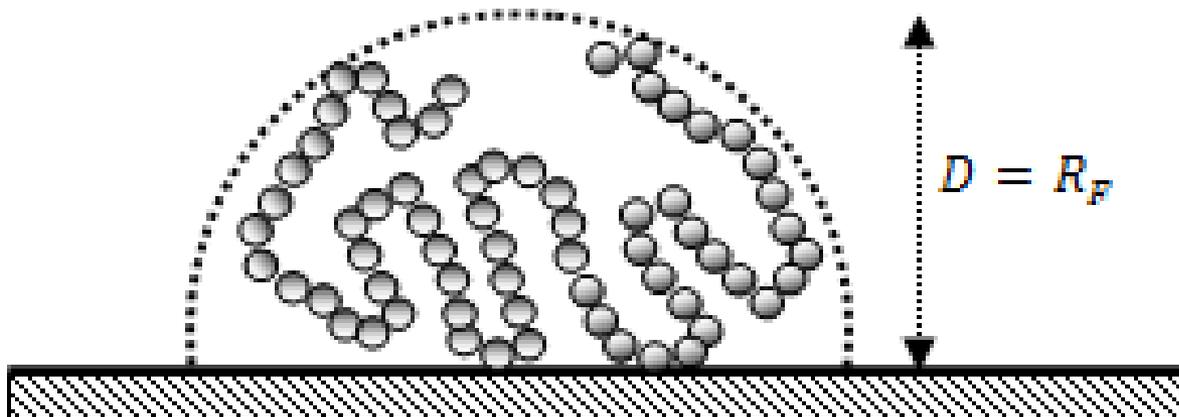


DILUTED BULK REGIME



□ Single chain

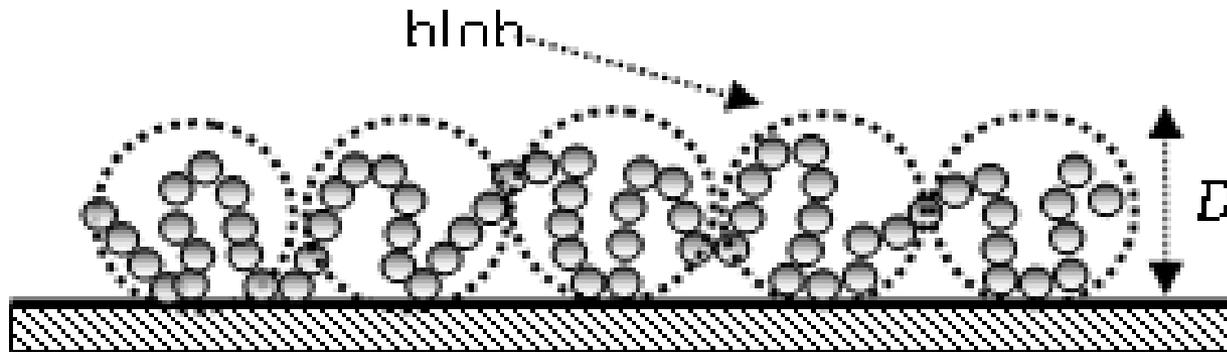
- It is assumed that each monomer is obtained an attractive $(-k_B T \delta)$ which promotes the phenomenon of adsorption. Two cases are discussed:
- If $\delta < \delta_c \sim N^{-3/5}$, entropic effects dominate and the adsorption is low. The dimensions of the coil parallel and orthogonal to the layer-surface remain of the same order as the three-dimensional Flory-radius $R_F \sim aN^{3/5}$



DILUTED BULK REGIME



- If $\delta > \delta_c$, the polymer-chain is adsorbed and expands on the surface and may be organized as a succession of blobs of the same size. The calculation of the characteristics of the blobs by using the scale laws gives: $D \sim a \delta^{-1}$ and $R_{\parallel} \sim aN^{3/4} \delta^{1/4}$



ADSORPTION ISOTHERM



□ dilute surface regime

- This regime appears for a volume fraction $0 < \varphi <$

$$\varphi_1 \sim N^{-1/2} \delta^{1/2} \exp(-N\delta^{5/3})$$

- Calculation of the area coverage has shown that it is proportional to the volume fraction φ : $\Gamma(\varphi) = \frac{1}{2} \delta^{-1} \varphi \exp(N\delta^{5/3})$

□ Bidimensionnel semi-dilute surface regime

- When $\varphi_1 < \varphi < \varphi_2 \sim \delta^{4/3} \exp(-N\delta^{5/3})$ the surface is in a two-dimensional semi-diluted regime and the coverage rate varies as in the case of the surface diluted regime : $\Gamma(\varphi) = \frac{1}{2} \delta^{-1} \varphi \exp(N\delta^{5/3})$

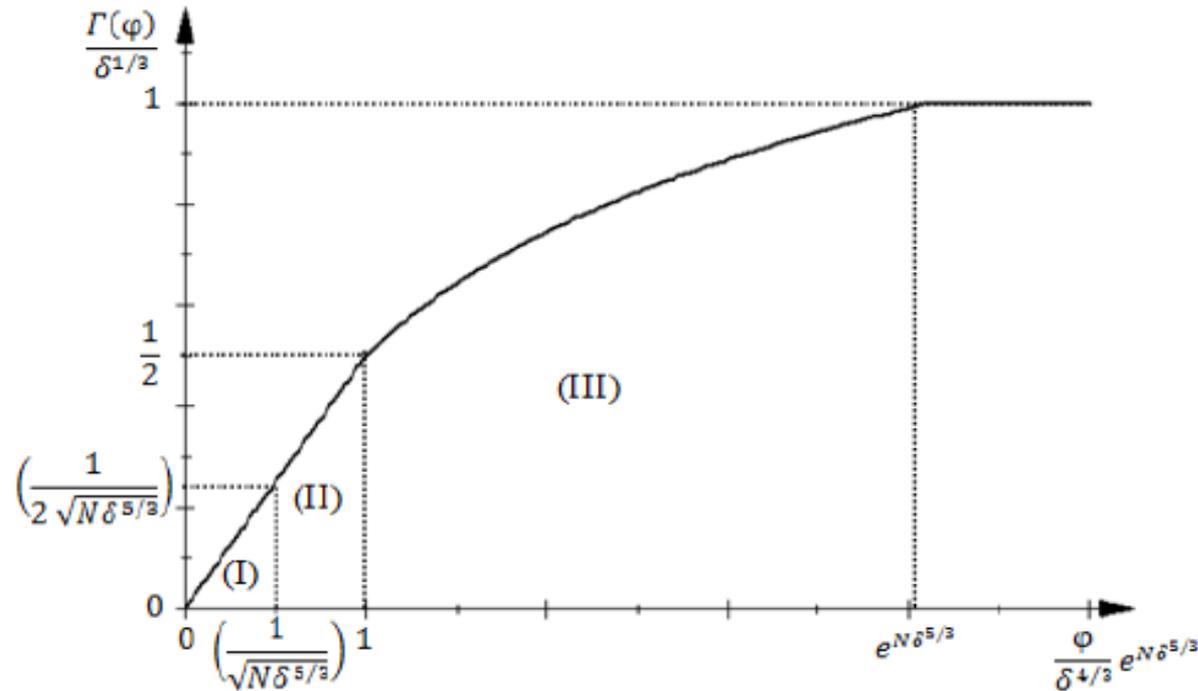
□ Plateau regime

- When the area coverage rate exceeds a critical value $\Gamma \sim \delta^{1/3}$ the surface is saturated and the coverage rate becomes independent of the volume fraction. A correction of this coverage rate gives: :

$$\Gamma(\varphi) = \delta^{1/3} \left(1 + \frac{1}{2N\delta^{5/3}} \ln \left(\varphi \delta^{-4/3} \right) \right)$$

the regime is called plateau regime defined in the interval $\varphi_2 < \varphi < \varphi_3 \sim \delta^{4/3}$

ADSORPTION ISOTHERM



- The figure shows the representation of the coverage rate as a function of the volume fraction. There is a strong adsorption for the first two regimes, diluted and semi-diluted surface, because of the presence of the exponential term in the expression of Γ .
- For the diluted regime (zone I), the surface is not saturated and there are enough sites for all the polymers. Polymer chains do not compete for

ADSORPTION ISOTHERM

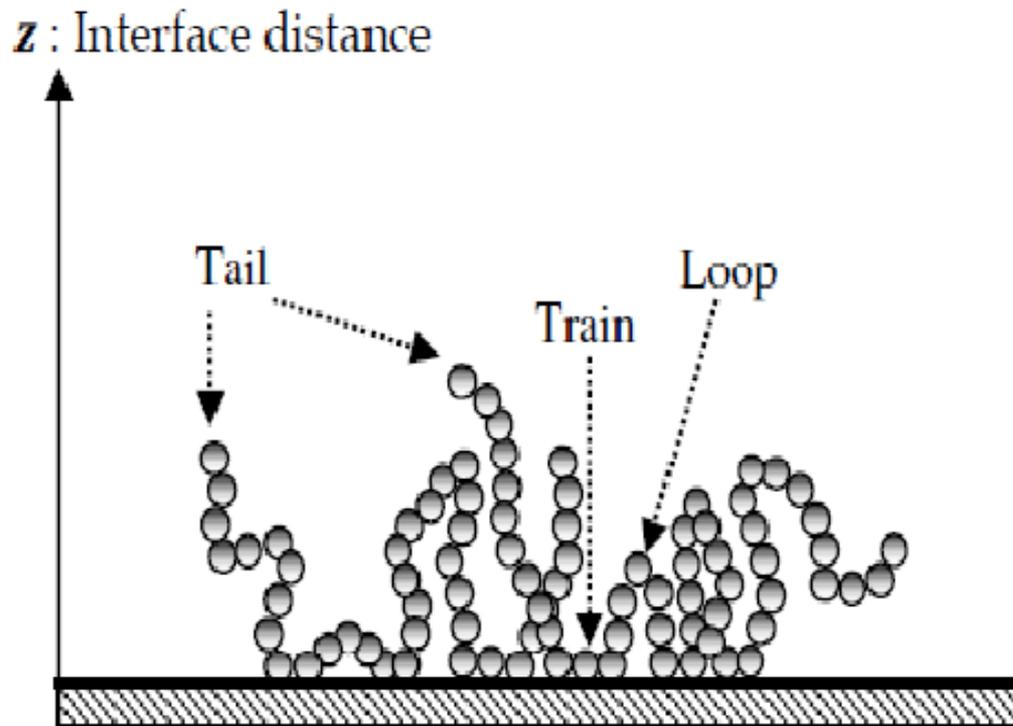


- When the concentration of polymer in solution increases, the surface becomes more and more saturated and the polymer chains compete to occupy the available sites (zone II).
- Due to the repulsive interactions induced (steric) by the monomers of the adsorbed polymers, the conformation adopted by the polymers changes.
- When exceeding a critical concentration of polymer in solution, a pseudo-plateau is reached. In this regime (zone III), the surface coverage rate increases only slightly when φ increases. This can be explained by the compensation between the attractive forces related to the affinity of the polymers for the surface and the repulsive forces between the monomers. So it's impossible for any additional polymer to adsorb, this is confirmed by the presence of the logarithmic term in the expression of Γ .
- At very high doses of polymer, the high osmotic pressure can force the adsorption of additional polymers.

DENSITY PROFILE



- The adsorption of a polymer on a surface causes a change in the conformation of the chain compared to its conformation in solution. That is to say, the adsorbed polymer does not form a uniform layer on the surface of the clay sheet. This is why we are interested in the calculation of the variation of the volume fraction (density profile) along the z axis.



DENSITY PROFILE



According to the scaling laws, the density profile of an adsorbed layer is divided into three regions:

❑ **Proximal region $a \ll z \ll D$**

- The density profile near the surface varies slowly due to the interaction between the monomers and the surfaces.
- It has been shown that for this region the volume fraction varies as: $\varphi(z) \sim \varphi_s \left(\frac{z}{a}\right)^{-1/3}$

❑ **Central region $D \ll z \ll R_F$**

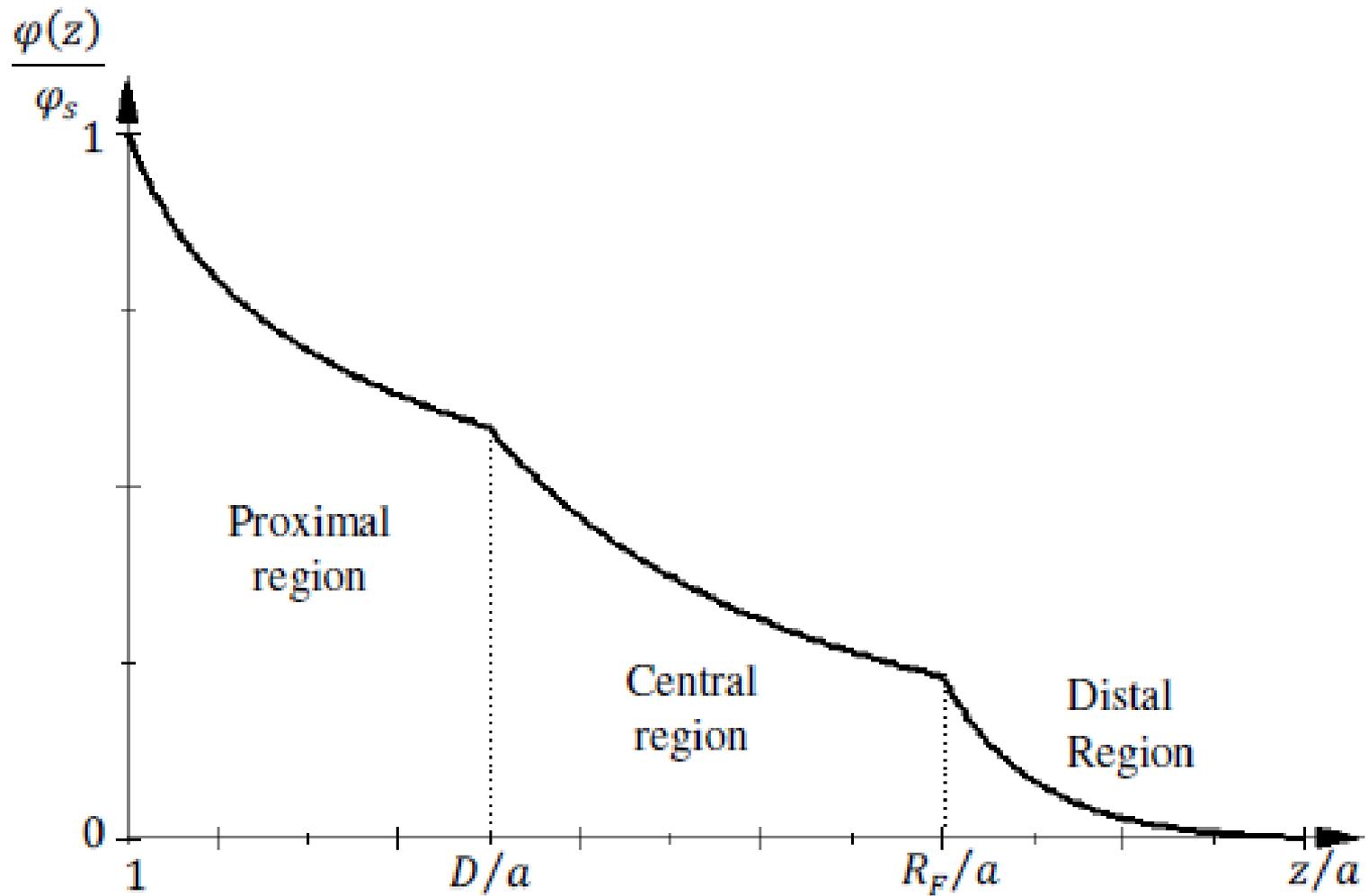
- The adsorbed layer is considered as a semi-dilute solution
- The volume fraction for this region is of the form: $\varphi(z) \sim \left(\frac{z}{a}\right)^{-4/3}$

❑ **Distal region $z \gg R_F$**

- In the distal region, the concentration profile decreases exponentially.
- Calculating the volume fraction for this region gives:

$$\varphi(z) = N^{-4/5} e^{(R_F - z)/a}$$

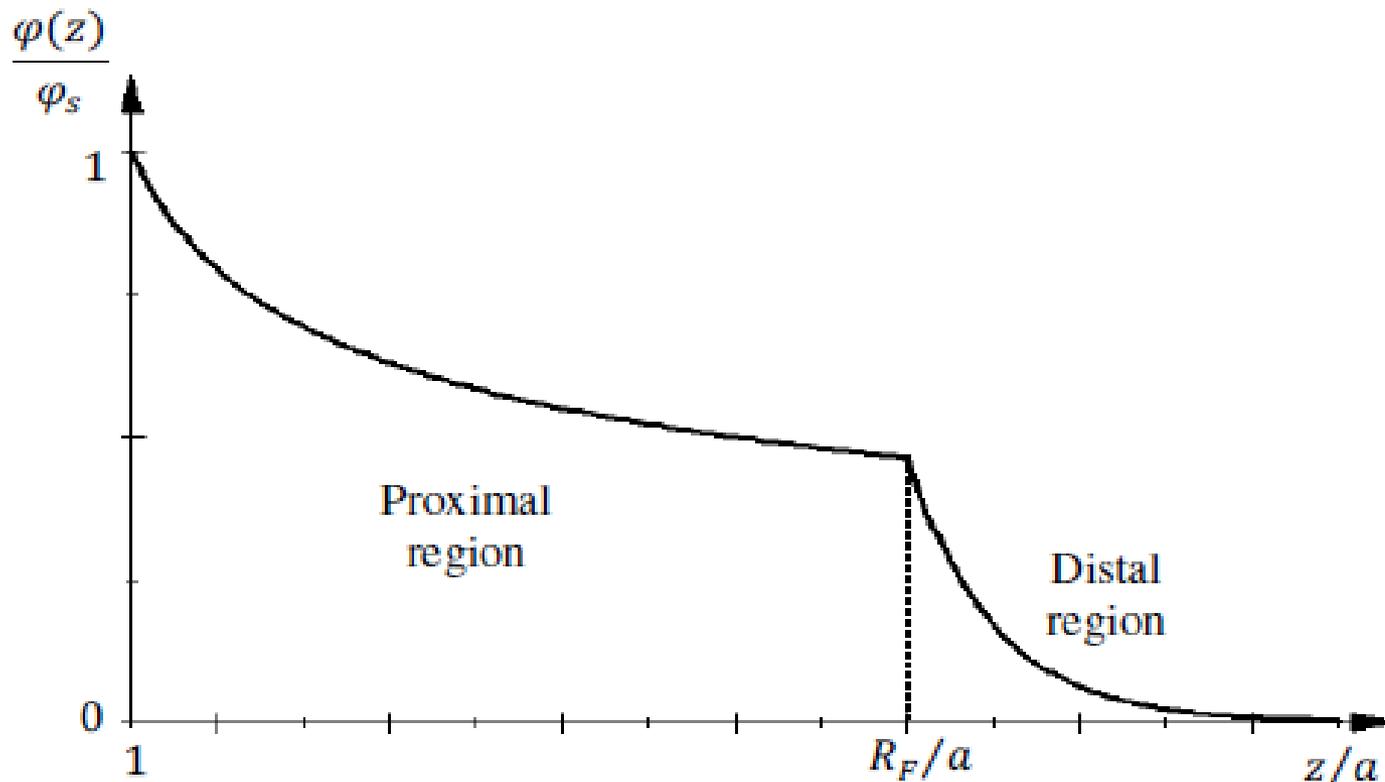
DENSITY PROFILE



DENSITY PROFILE



- for $\delta \gg \delta_c$, we note the existence of three zones (proximal, central and distal) with different volume fractions.
- But when $\delta = \delta_c$, the central region disappears and there are only two region: proximal and distal.



CONCLUSION



- The monitoring of the evolution of the coverage rate in bulk diluted regime showed that for the two systems diluted and semi-diluted on the surface the coverage rate increases rapidly with the increase in the volume fraction, which reflects the strong chain adsorption because of the availability of sites at the adsorption surface.
- As soon as the sites available on the surface are mainly occupied, the attraction of the surface towards the chains decreases and the coverage rate of surface increases only logarithmically and tends towards saturation, this regime is called plateau regime, the bulk is always diluted.
- The variation of volume fraction in monomer (density profile) at the surface as a function of the orthogonal to the adsorption plane showed the existence of three zones (proximal, central and distal) with different volume fractions. The proximal zone is characterized by the contact between the chain and the surface, due to the strong attraction between the two.

**THANK YOU
FOR YOUR
ATTENTION**