

# Biopolymères

Ma12- Cyrille Vézy - T207 - L2n



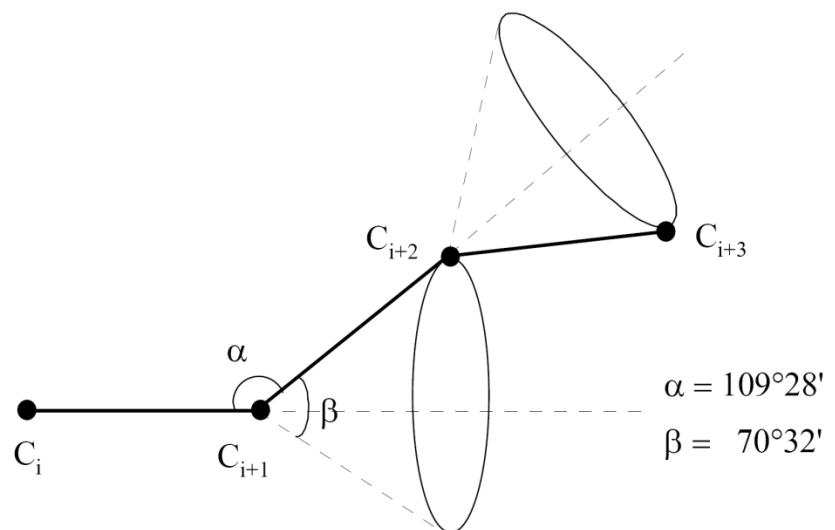
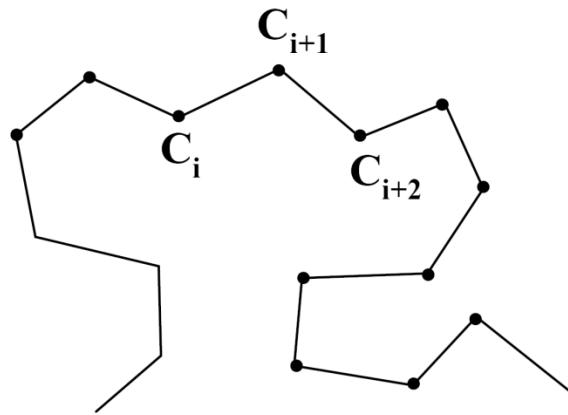
# La chaîne idéale

- Quelle est la taille,  $R$ , que prend une chaîne de polymère?
- Soit  $N$  monomères de taille  $a$ :
  - 1922 : Staudinger pense que la configuration est un bâton et donc  $R=Na$
  - 1940 : Kuhn démontre qu'en fait on a une pelote à cause de la libre rotation autour des liaisons C-C

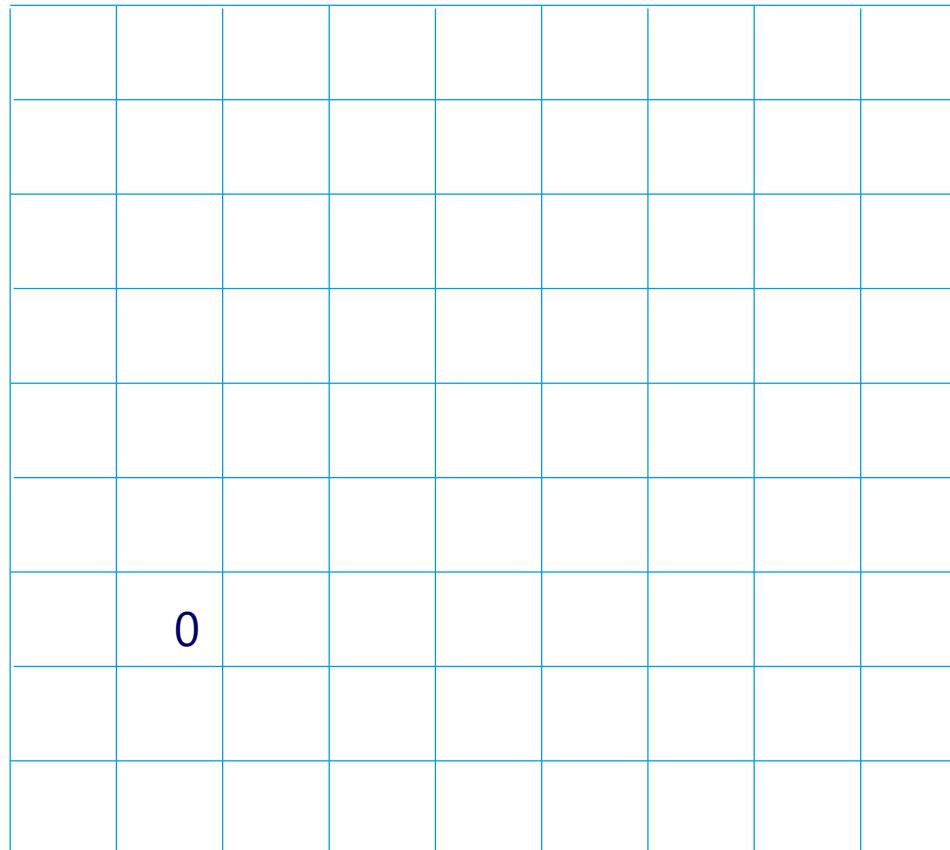
# La chaîne idéale

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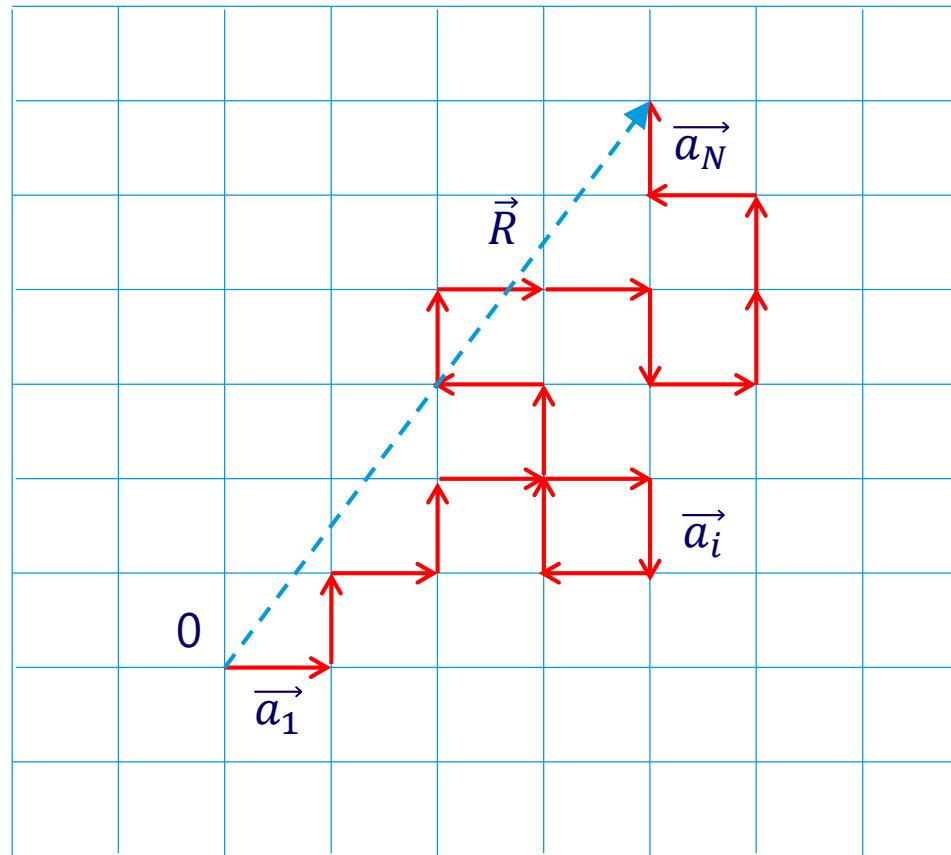
# La chaîne idéale



# Marche aléatoire



# Marche aléatoire



# Calcul de la distance bout à bout $\overrightarrow{R}$

On a N monomères de taille  $a$

$$\overrightarrow{R} = \sum_{i=1}^N \overrightarrow{a_i} \quad \text{or on a une marche aléatoire donc}$$

$$\langle \overrightarrow{a_i} \rangle = 0$$

# Calcul de la distance bout à bout $\overrightarrow{R}$

On va donc calculer la distance quadratique moyenne  
elle donne la distance typique parcourue

$$\langle \overrightarrow{R}^2 \rangle = \sum_{i,j=1}^N \langle \overrightarrow{a_i} \cdot \overrightarrow{a_j} \rangle$$

On obtient aisément que :

$$\langle \overrightarrow{R}^2 \rangle = Na^2$$



# Calcul de la distance bout à bout $\overrightarrow{R}$

et donc la taille de la pelote est donnée par l'expression suivante:

$$R_G = (\langle \vec{R}^2 \rangle)^{1/2} = N^{1/2}a$$

On l'appelle rayon de giration : taille typique du polymère



# Pelote gaussienne

- A présent on va calculer la probabilité que la chaîne parte de 0 et arrive au point  $\vec{R}$  :

$$P(\vec{R}) = \frac{\Gamma_N(\vec{R})}{(2d)^N}$$

Or  $\vec{R}$  c'est la somme d'un grand nombre de variables aléatoires indépendantes ( $10^3$  à  $10^5$ )

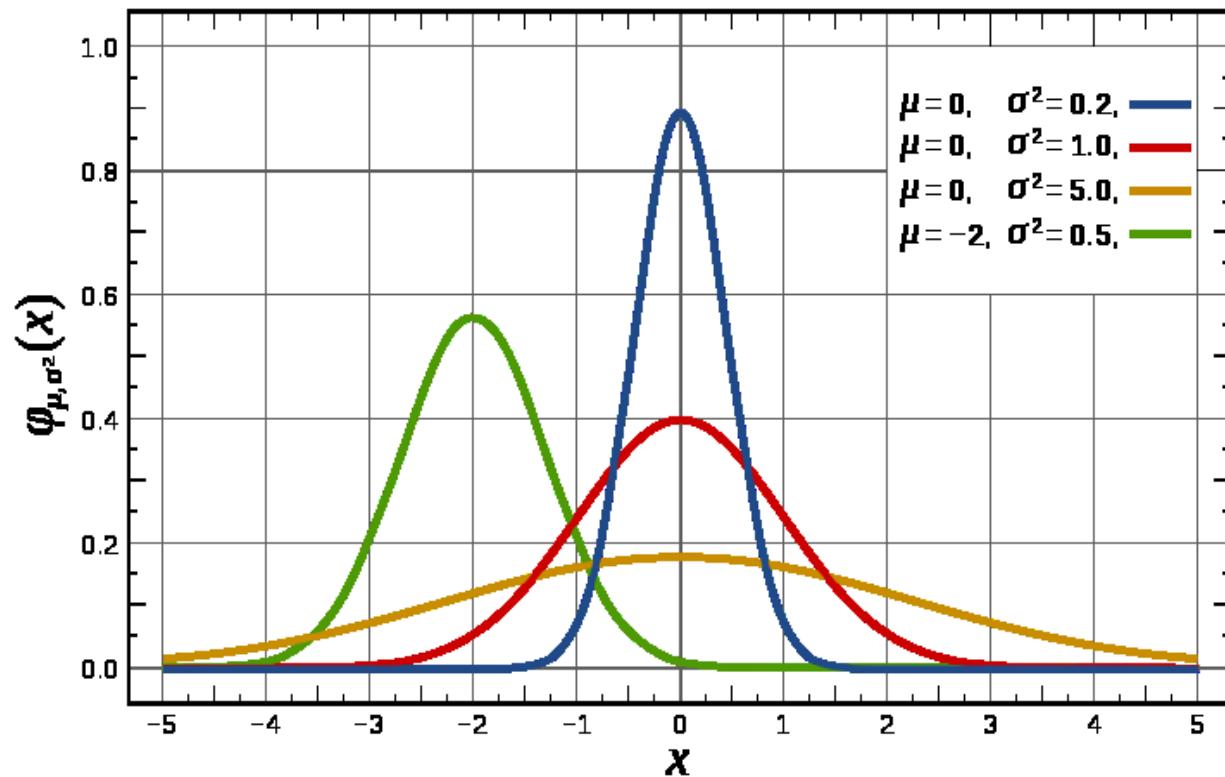
# Pelote gaussienne

- Cette probabilité doit suivre une loi normale d'après le théorème central limite
- [https://interstices.info/jcms/int\\_69164/la-simulation-de-monte-carlo](https://interstices.info/jcms/int_69164/la-simulation-de-monte-carlo)



# Pelote gaussienne

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$



# Pelote gaussienne

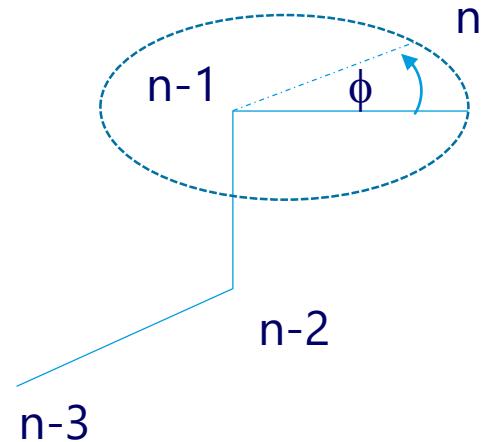
- La probabilité que la chaîne parte de 0 et arrive au point  $\vec{R}$  vaut:

$$P(\vec{R}) = \left( \frac{3}{2\pi Na^2} \right)^{3/2} \exp \left( -\frac{3\vec{R}^2}{2Na^2} \right)$$

C'est une loi gaussienne ou normale

# Longueur de persistance $l_p$

**Cas discret** : on considère une chaîne d'atomes



# Longueur de persistance $l_p$

La chimie quantique montre qu'il y a trois positions possibles

$\phi = 0$  configuration trans état d 'énergie minimale

$\phi = +/- \pi/3$  configuration gauche qui sont des états métastables

Petit rappel :  $k_B T = 0,025$  eV

# Longueur de persistance $l_p$

Il y a donc activation thermique pour passer d'une configuration trans à une configuration gauche.

$$\text{La longueur typique } l_p = a \cdot \exp\left(\frac{\Delta E}{k_b T}\right)$$

Si  $l < l_p$ : très peu de défauts sur la longueur de la chaîne  
= rigide

Si  $l > l_p$ : souple

# Longueur de persistance $l_p$

**Cas continu :**

$l_p$  est relié à la rigidité de flexion du polymère qui peut être vu comme une tige.

Courber ça coûte de l'énergie :

$$E = \kappa \cdot \frac{1}{2} \int dS \frac{1}{R^2}$$

On peut approximer localement la courbure par une parabole et on montre que :

$$l_p = \frac{\kappa}{k_B T}$$

# Chaîne gonflée

- On doit prendre en compte un terme de volume exclu :  $\nu$
- Pour la chaîne idéale  $\nu$  gaussienne vaut  $1/2$  et  $R_G = N^\nu a$  et il dépend de la dimension de l'espace.



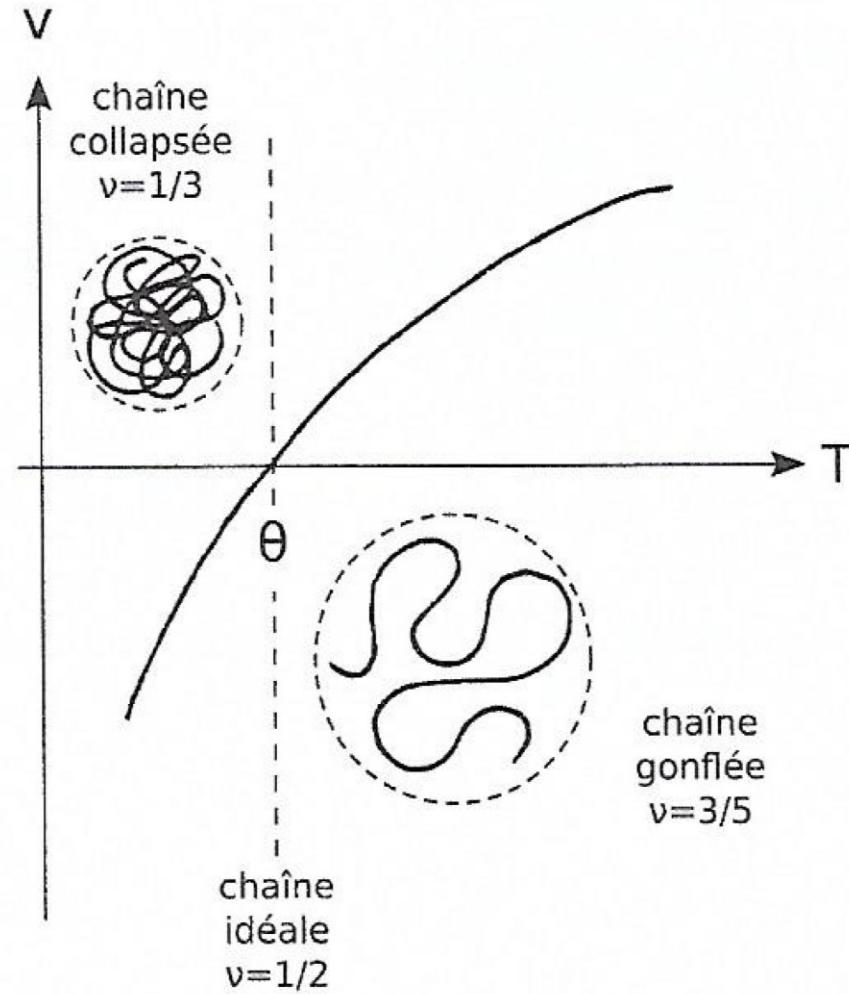
# Chaîne gonflée

- Il est relié au potentiel d'interaction entre les monomères

$$v(T) = \int \left( 1 - \exp \left( \frac{V(R)}{k_B T} \right) \right) d^3r$$

avec  $V(R)$  le potentiel d'interaction entre monomère





# Cellule eucaryote animale

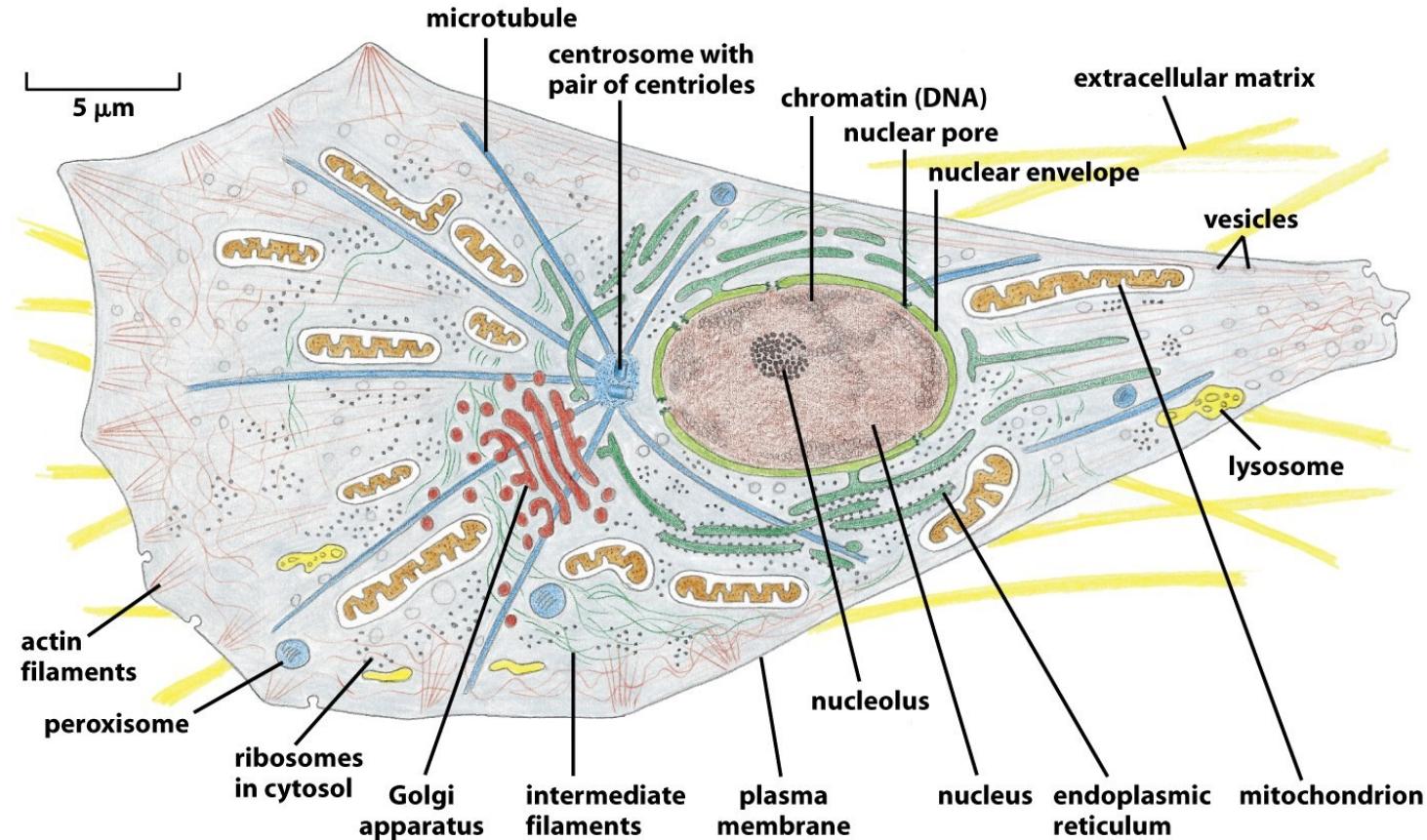


Figure 1-30 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Membrane cellulaire

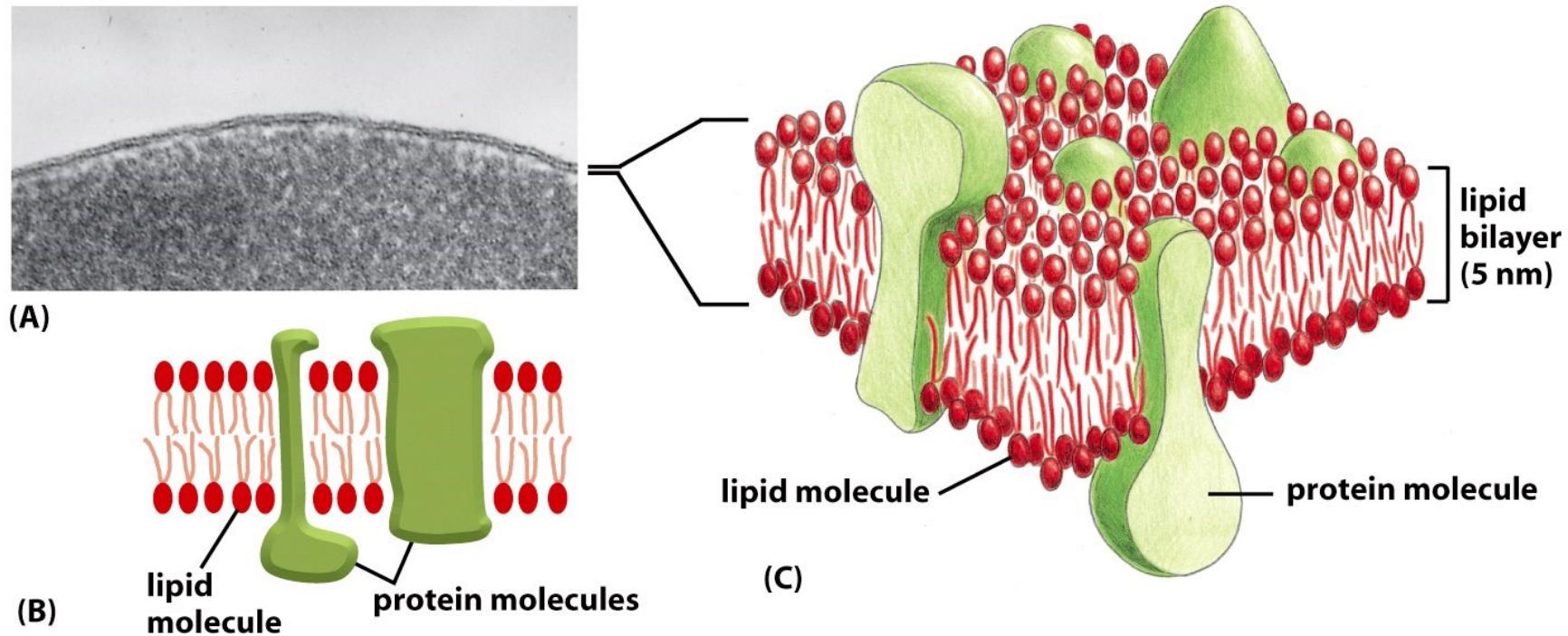
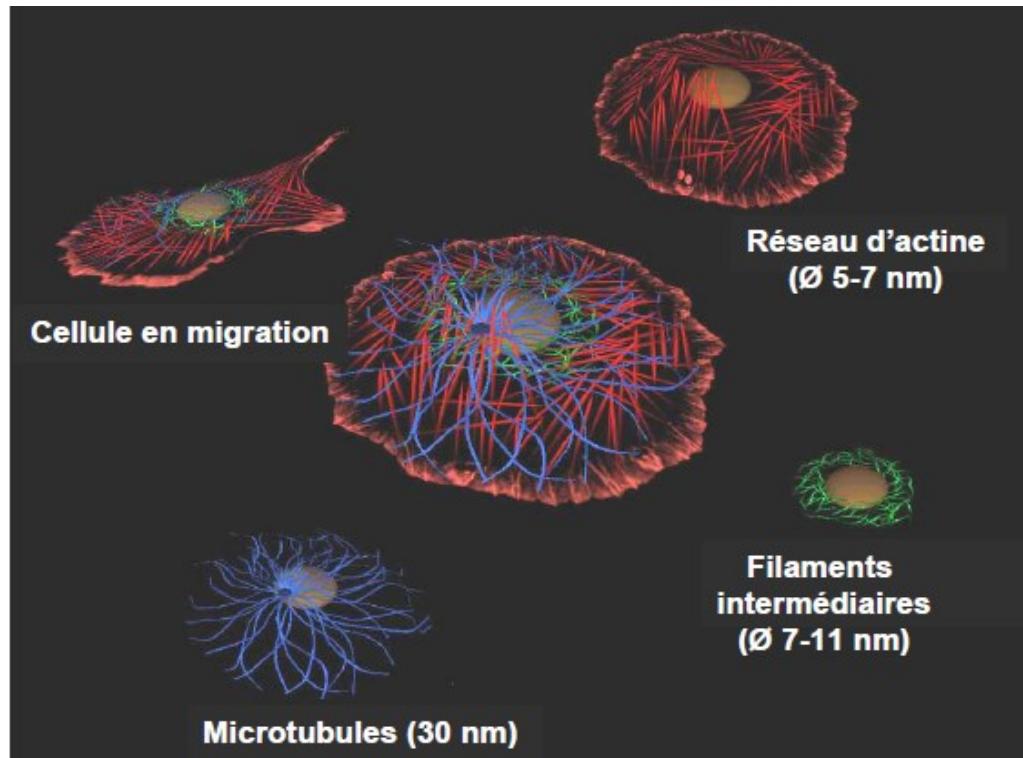
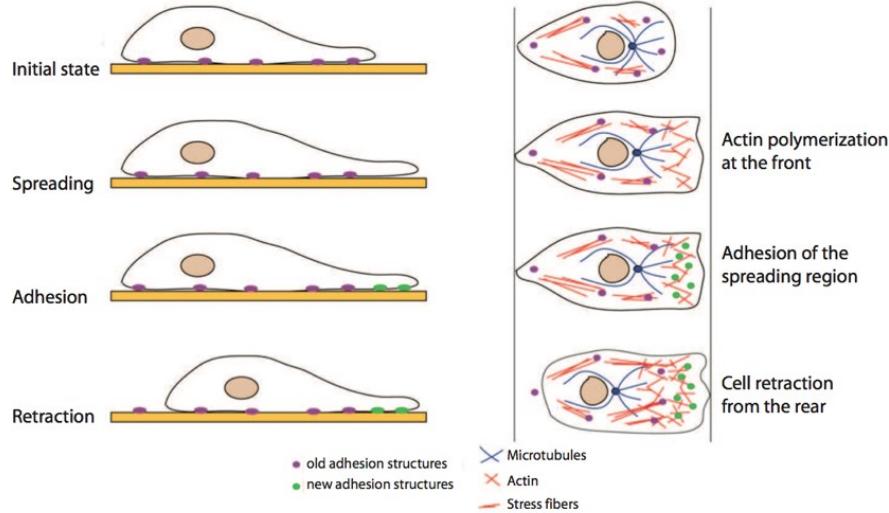


Figure 10-1 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Le cytosquelette



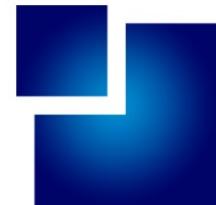
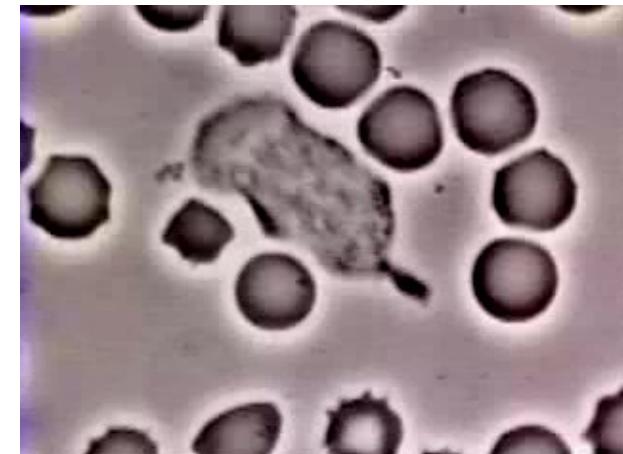
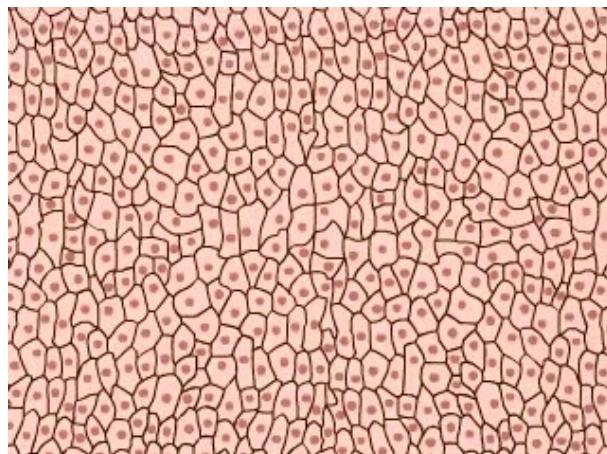
# La migration cellulaire



# La migration cellulaire: importance

## ▪ *Physiologique:*

- **développement embryonnaire** : migration en des endroits spécifiques pour la morphogénèse des organes et tissus
- **cicatrisation**: réparation de tissu endommagé
- **vascularisation**: cellules migrent pour former des réseaux de capillaires lors de l'angiogénèse
- **réponse inflammatoire**: migration des leucocytes vers les sites infectés



# La migration cellulaire: importance

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# La migration cellulaire: importance

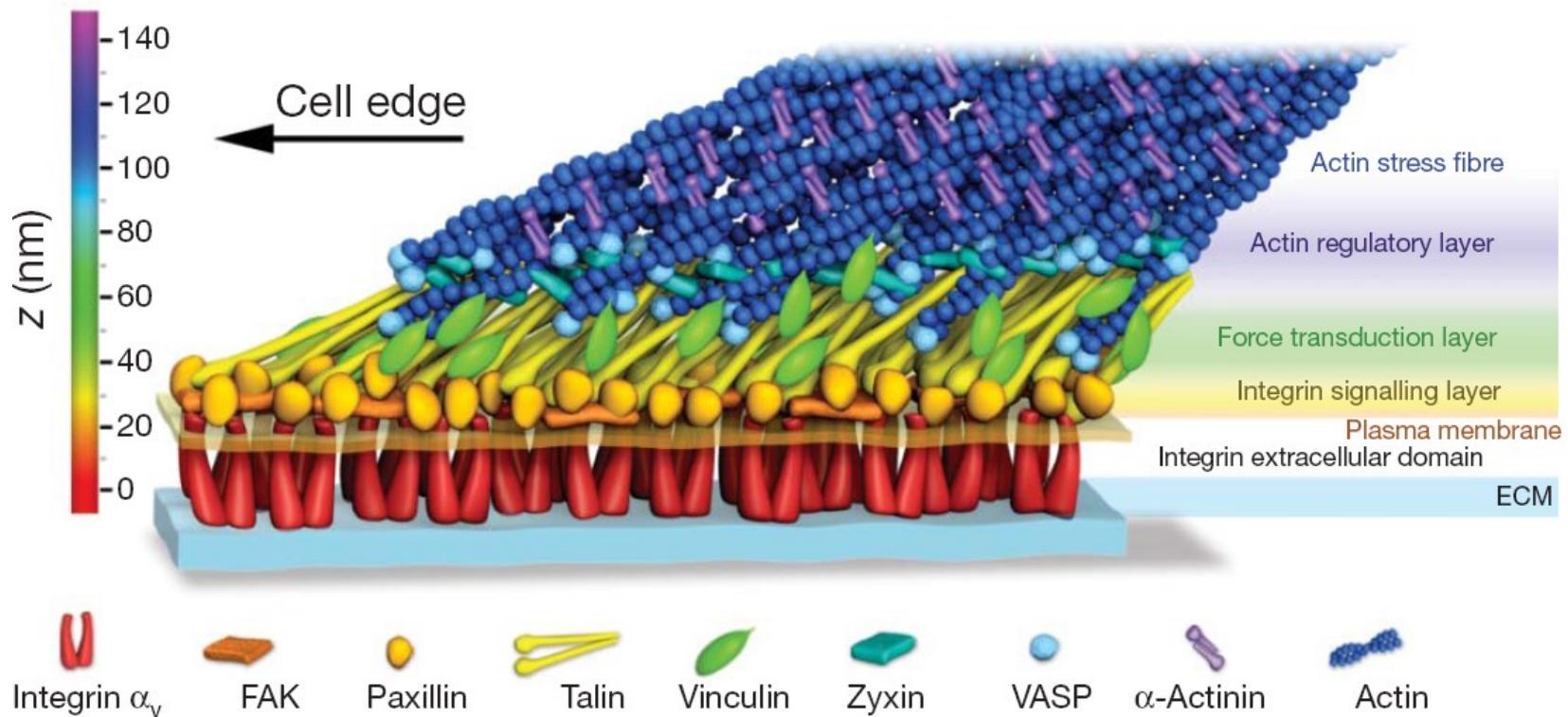
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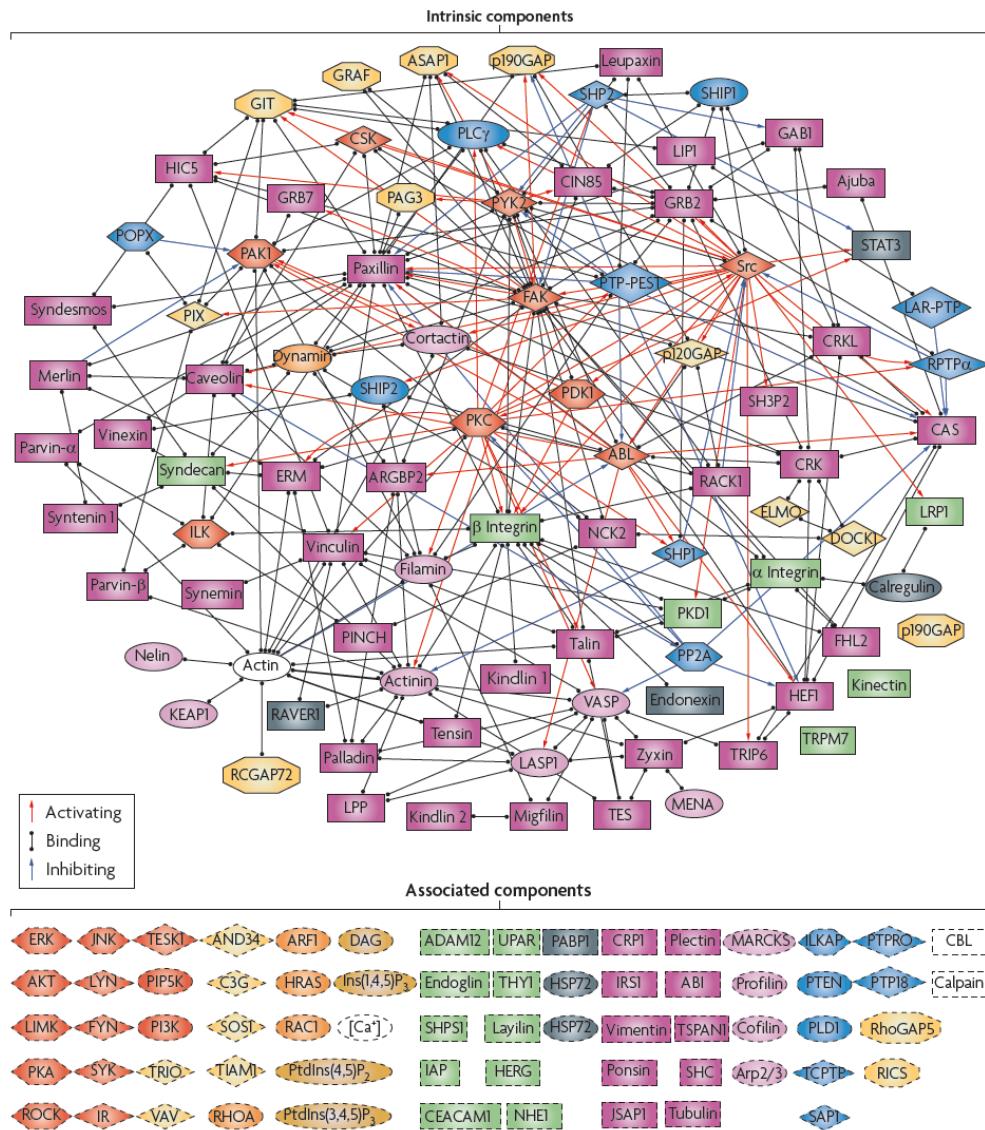
## ▪ ***Pathologique:***

- **vascularisation tumorale**: migration des cellules endothéliales vers la tumeur
- **metastatisation des cancers**: migration des cellules tumorales de la tumeur primaire via le réseau sanguin
- **croissance tumorale**: dérèglement de la prolifération cellulaire et du comportement migratoire

# La migration cellulaire: importance



Nature 468 (2010) p580



# ATP

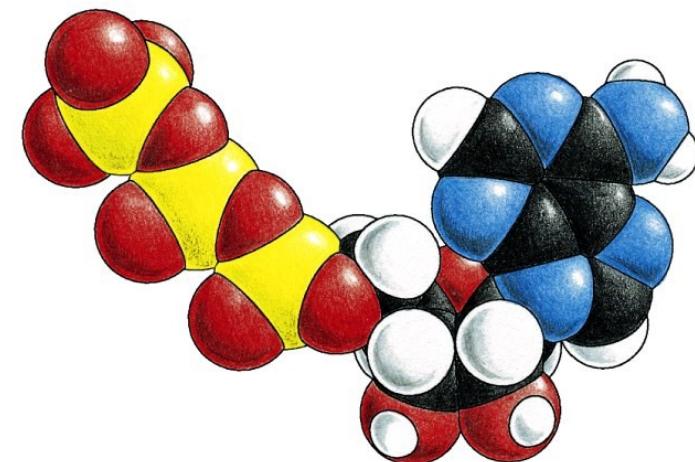
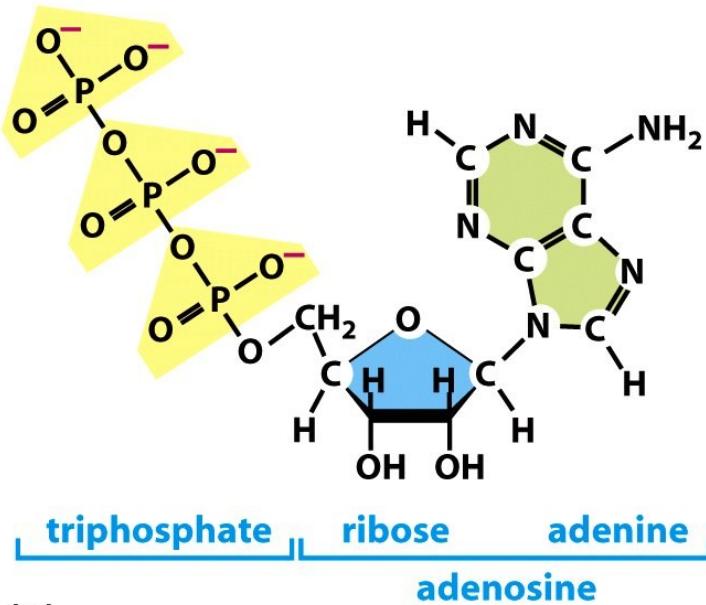


Figure 2-26 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# ATP

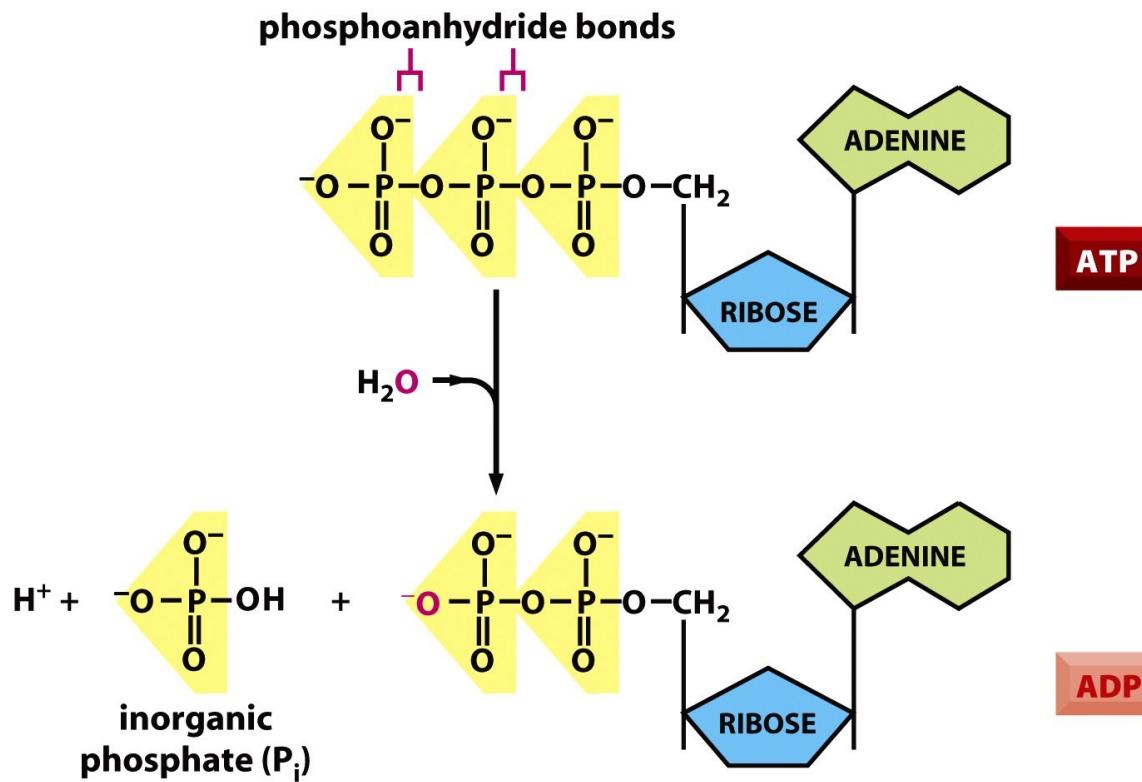
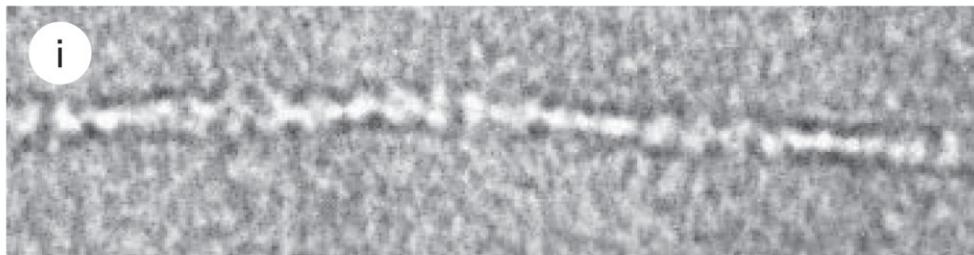


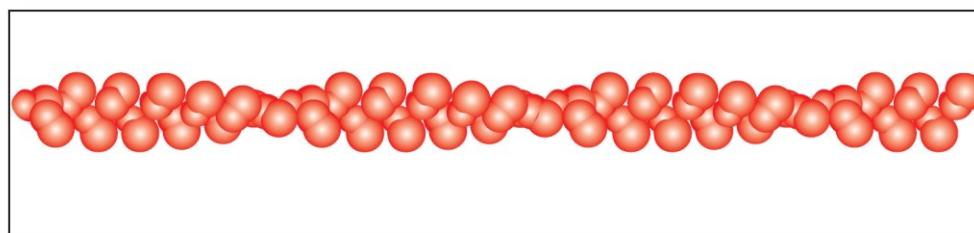
Figure 2-57 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Les filaments d'actine

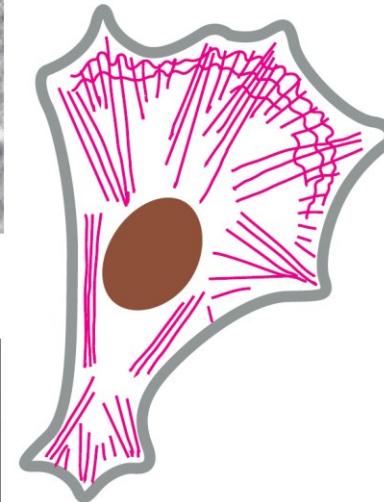
- Filament avec un  $l_p = 10 \mu\text{m}$  et un diamètre de 7 nm
- C'est donc un filament semi flexible



100 nm



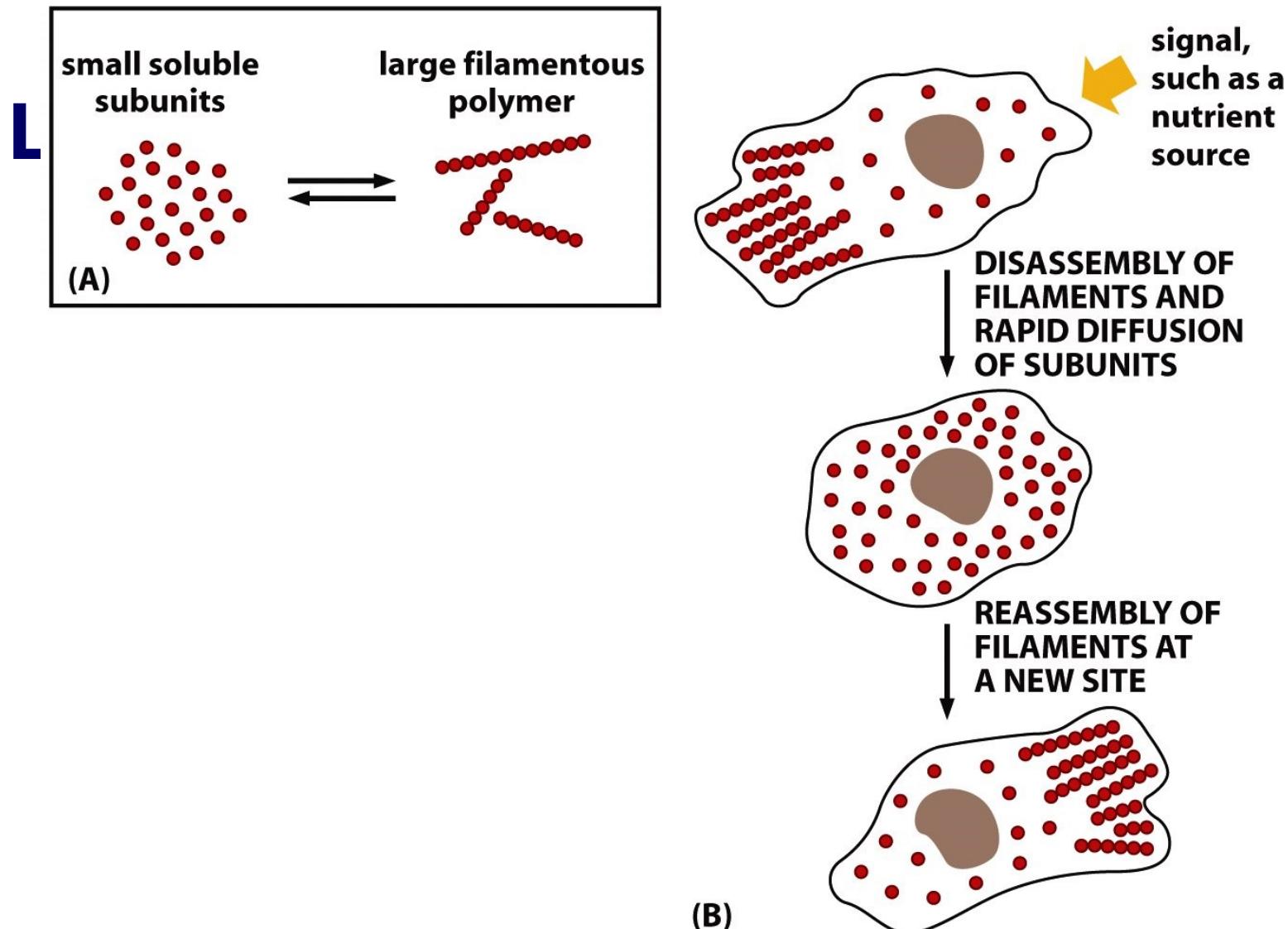
25 nm



# Les filaments d'actine

- C'est donc une double hélice
- Deux formes :
  - l'actine G (globulaire) qui est associée à une molécule d'ADP ou d'ATP
  - l'actine F (filament) construit à partir de l'actine G et un pas typique de l'hélice vaut 37 nm
- Vitesse de polymérisation 10aines de  $\mu\text{m}/\text{min}$





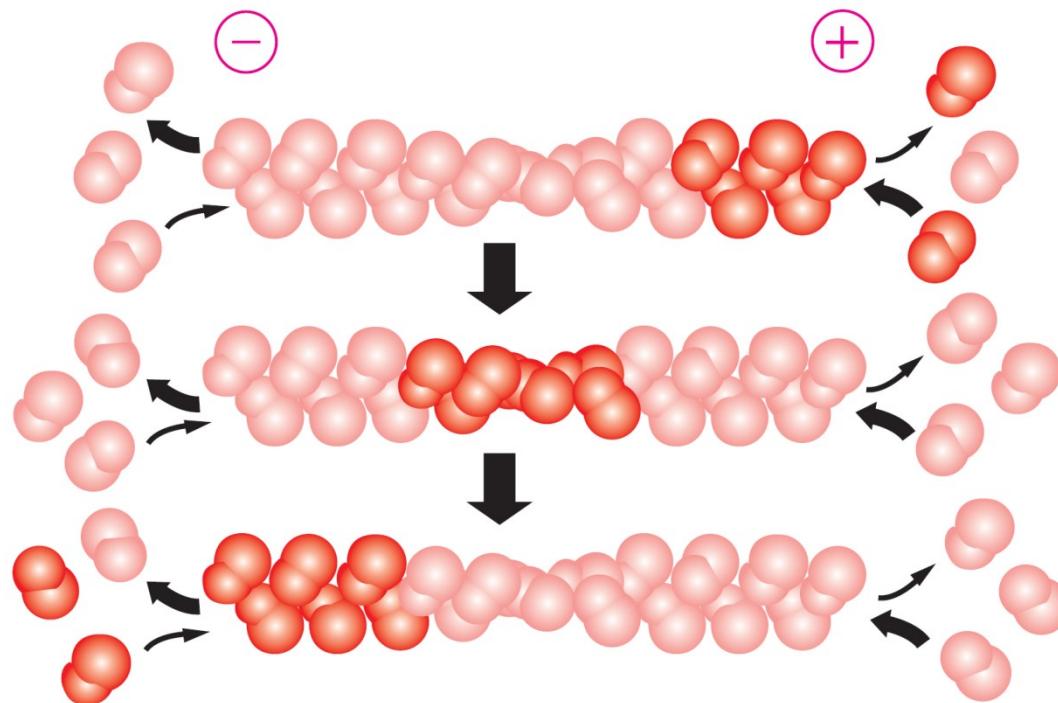
# Polymérisation de l'actine

- Pour former des filaments il faut polymériser l'actine G:
  - Actine G se fixe à l'ATP
  - Actines G-ATP se fixe entre elles : polymérisation
  - ATP s'hydrolyse en ADP
  - Dépolymérisation des Actines G-ADP

Mouvement de treadmilling



# Polymérisation de l'actine



# Polymérisation de l'actine



Soit  $k_{\text{on}}$  et  $k_{\text{off}}$  les constantes cinétiques d'associations et de dissociations

Calculons à présent  $\frac{d[P_N]}{dt}$

# Polymérisation de l'actine

$$\frac{d[P_N]}{dt} = k_{\text{on}}[P_{N-1}] \cdot [P_1] + k_{\text{off}}[P_{N+1}] - (k_{\text{on}}[P_N] \cdot [P_1] + k_{\text{off}}[P_N])$$

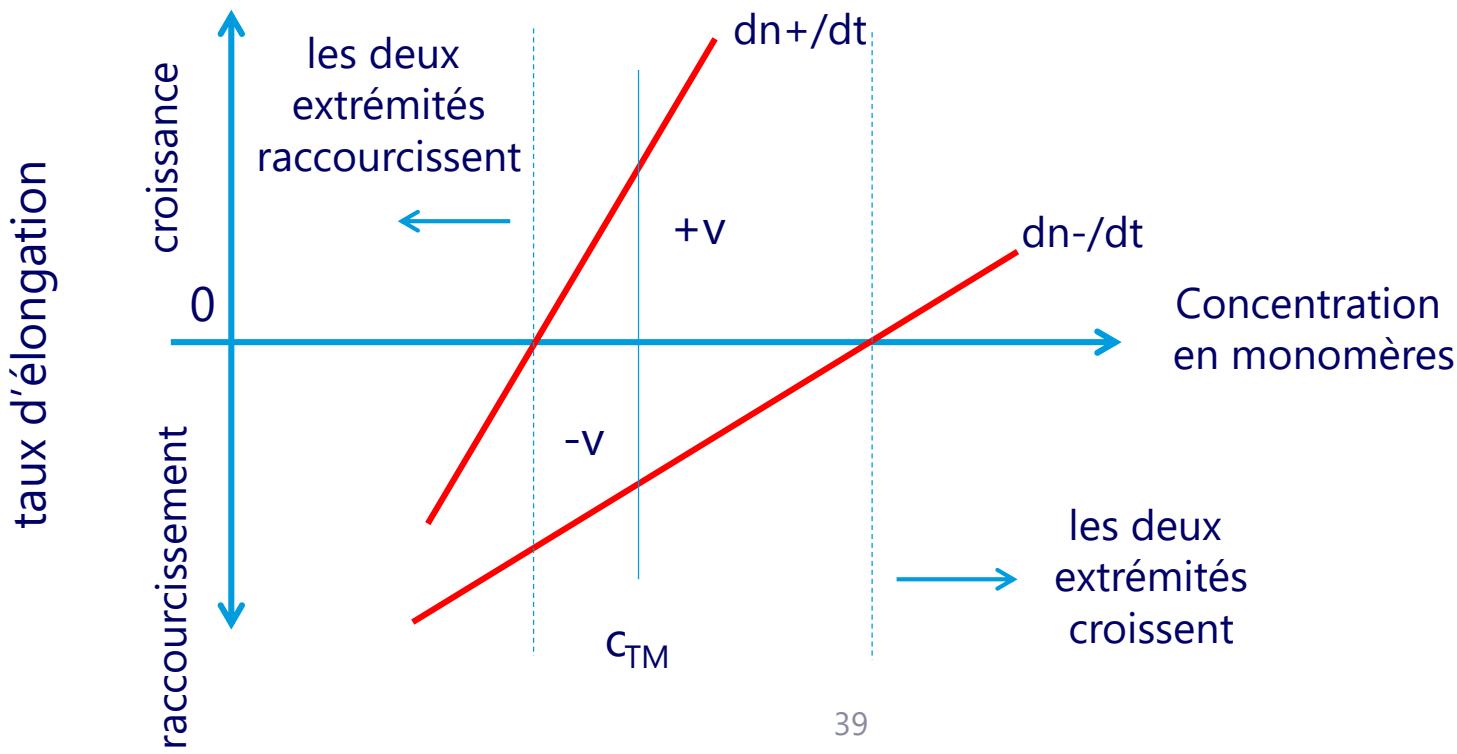
Soit  $\langle n \rangle$ , la valeur moyenne de la longueur d'un filament d'actine, alors

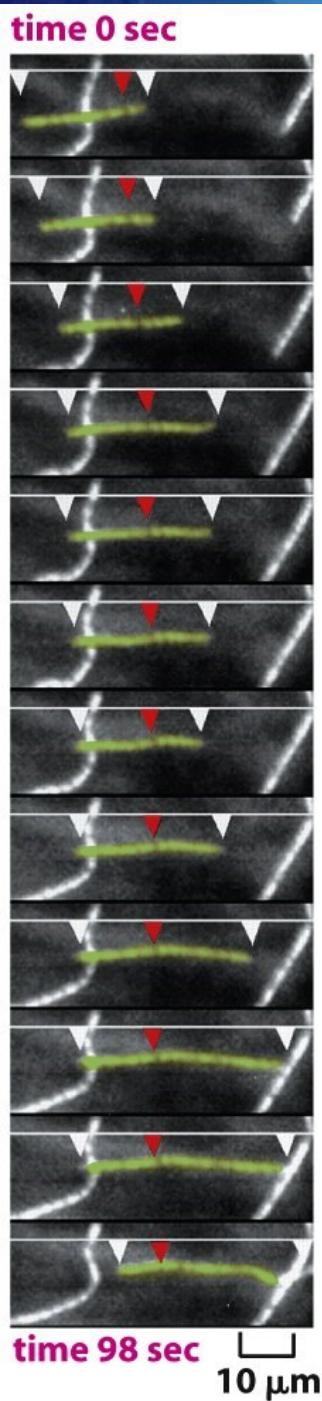
$$\frac{d\langle n \rangle}{dt} = k_{\text{on}} \cdot [P_1] - k_{\text{off}}$$

On peut donc avoir deux cas

# Polymérisation de l'actine

On a deux extrémités différentes

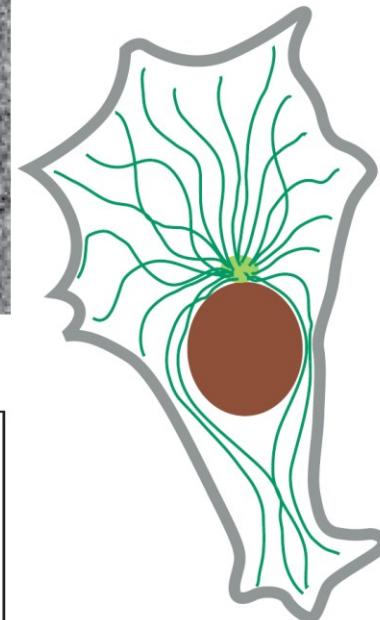
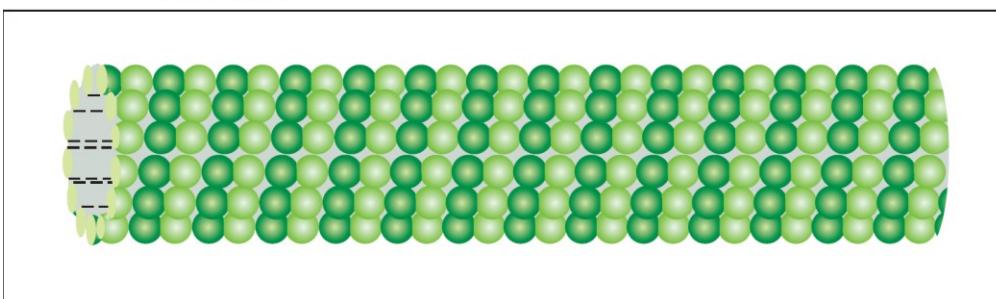
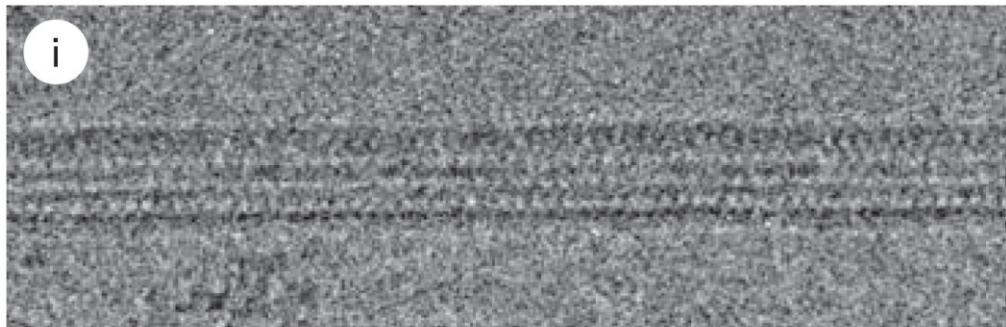




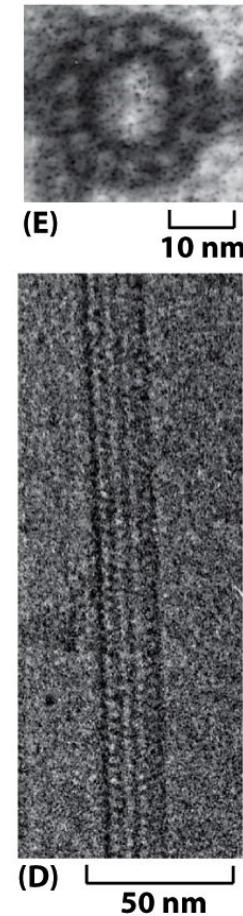
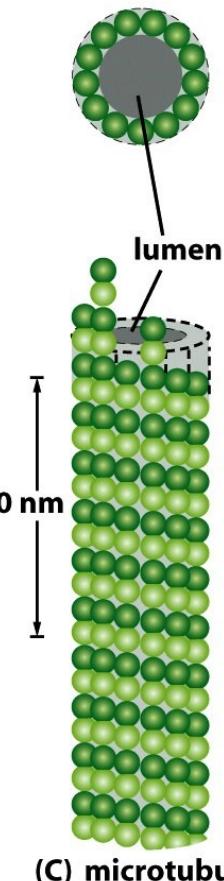
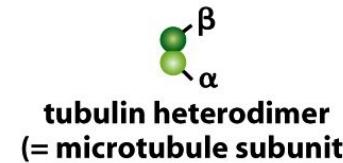
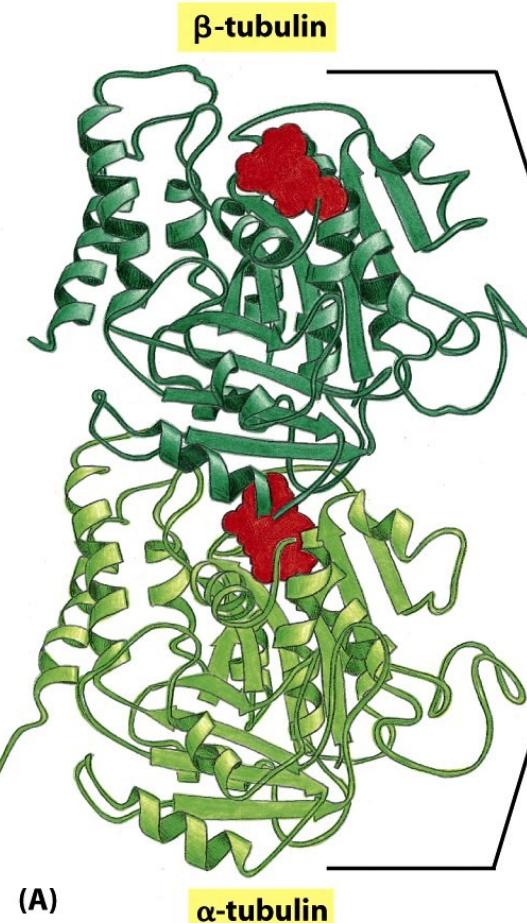
## Les biopolymères

# Les microtubules

- Tubes d'un diamètre de 21 nm et une  $I_p = 5$  mm



# Les microtubules



# Instabilité dynamique

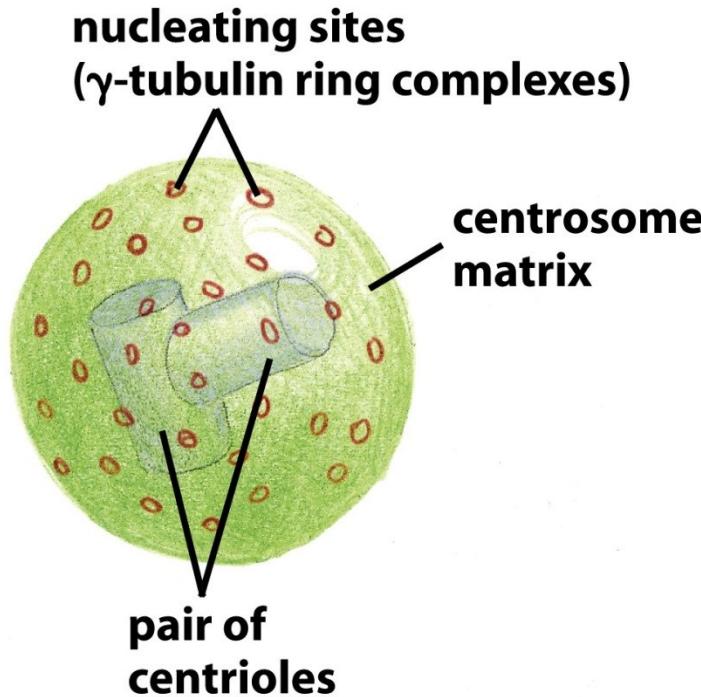


Figure 16-30a Molecular Biology of the Cell 5/e (© Garland Science 2008)

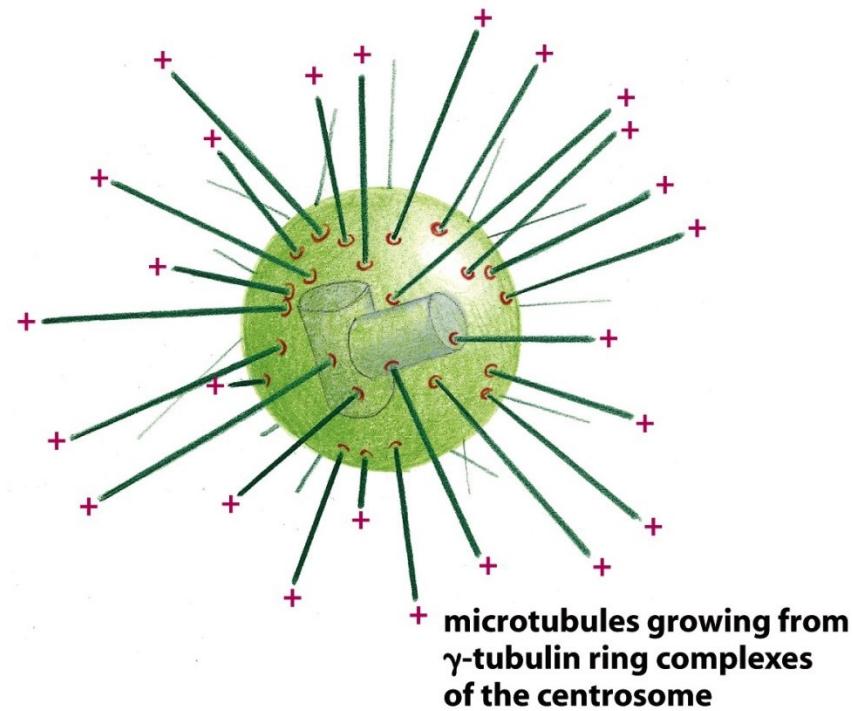


Figure 16-30b Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Instabilité dynamique

- Les dimères de tubuline se lient à des molécules de GTP (Guanosine Tri Phosphate) ou de GDP.
- On a plus de GTP à l'extrémité + et de GDP à l'extrémité –
- Vitesse de polymérisation =  $\mu\text{m/s}$



# Instabilité dynamique

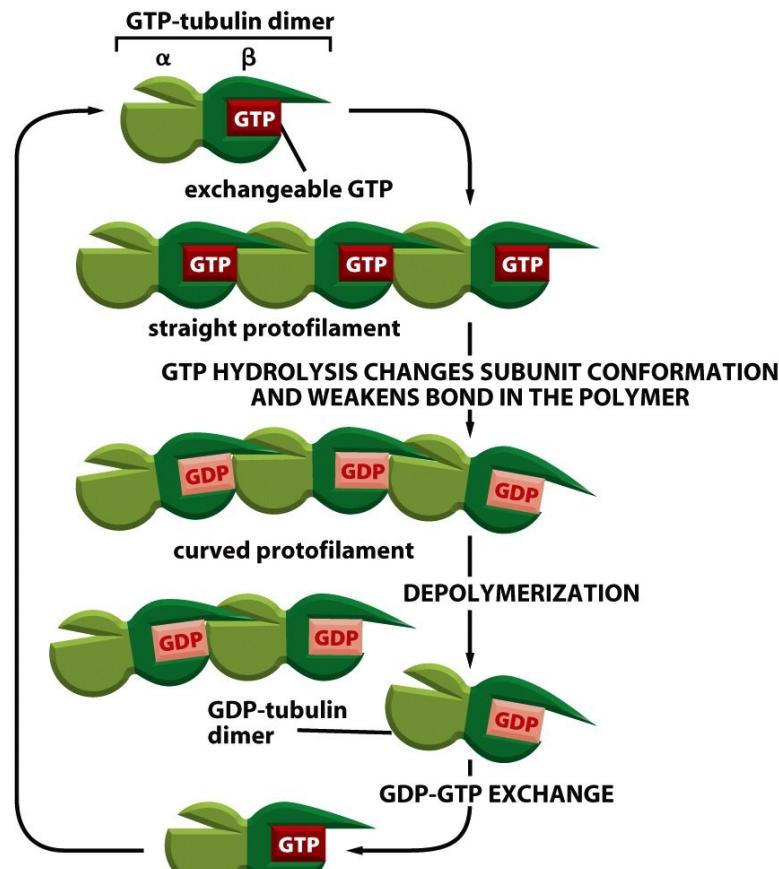
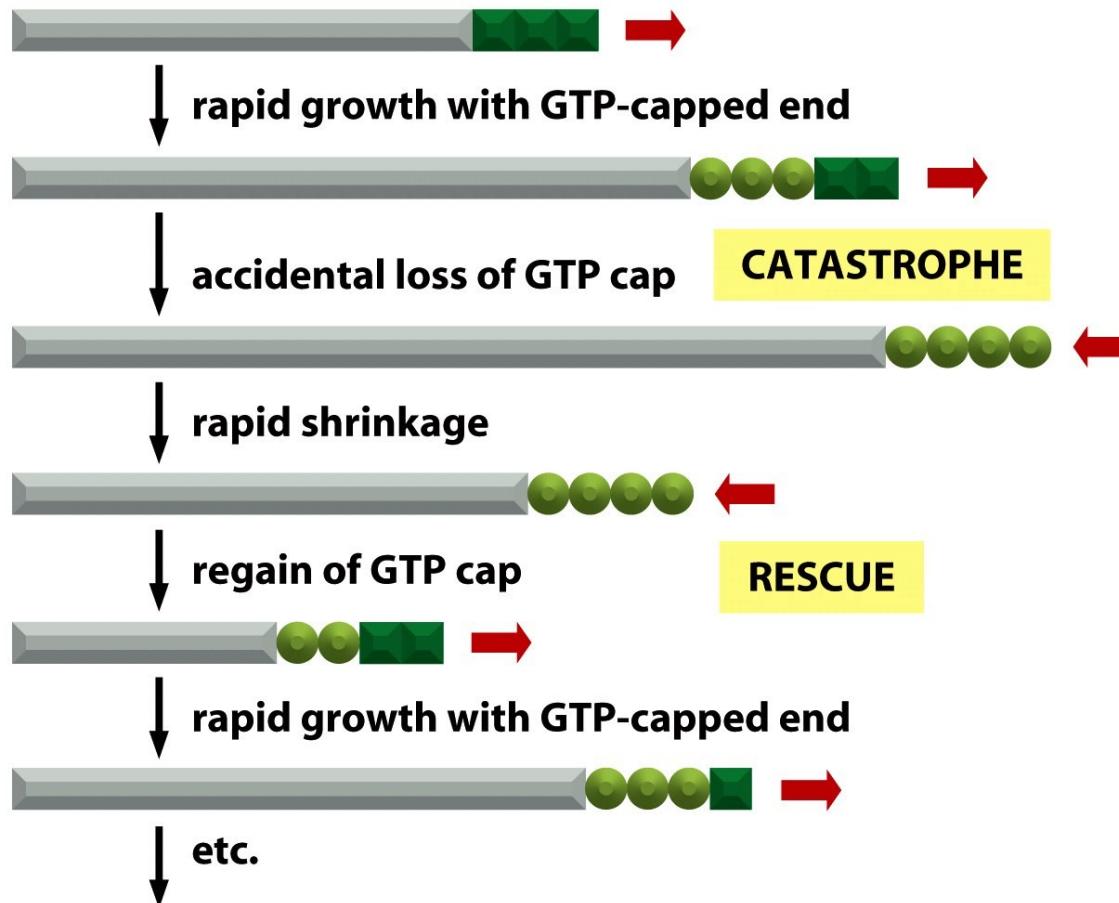
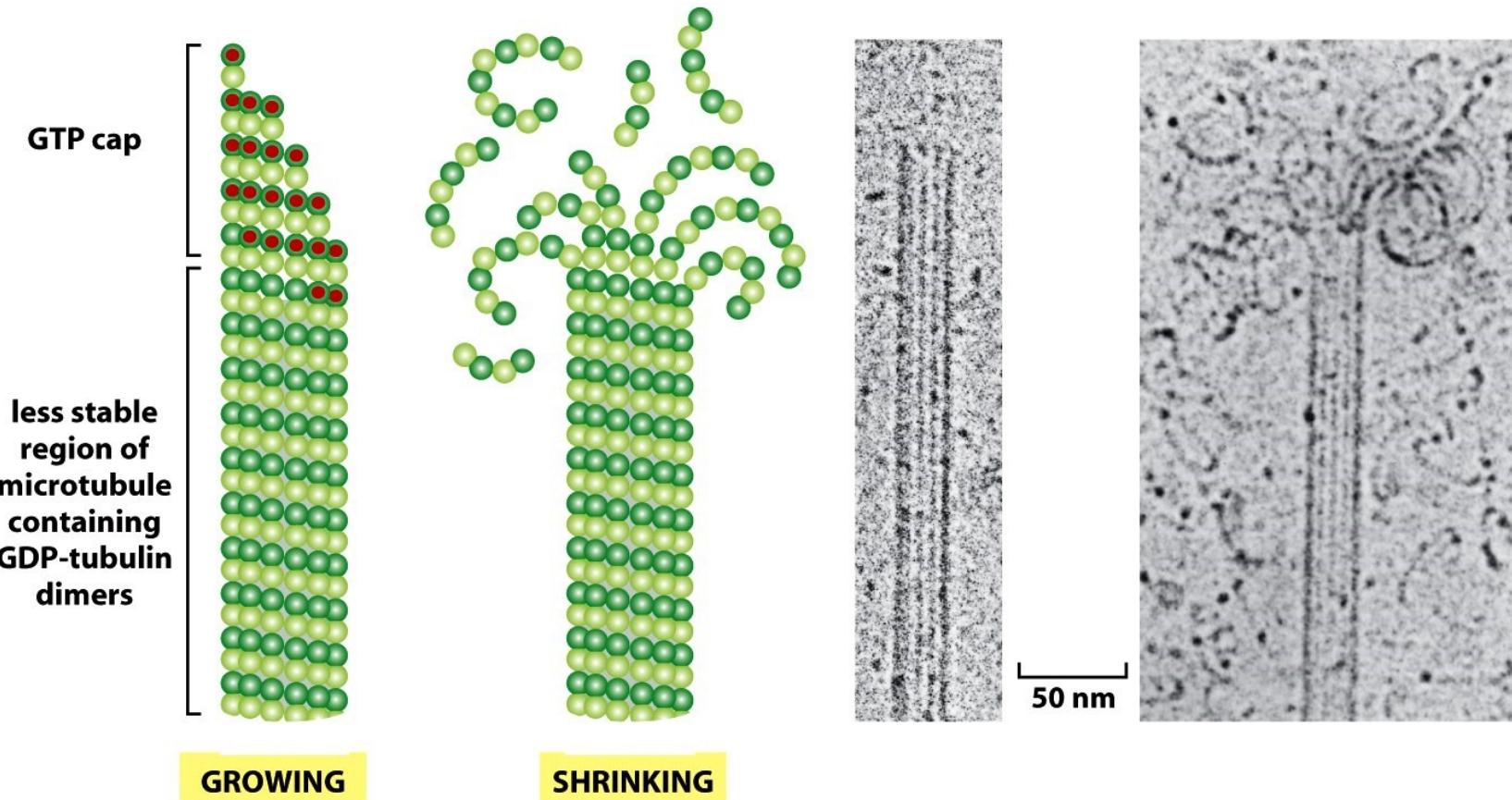


Figure 16-16b Molecular Biology of the Cell 5/e (© Garland Science 2008)

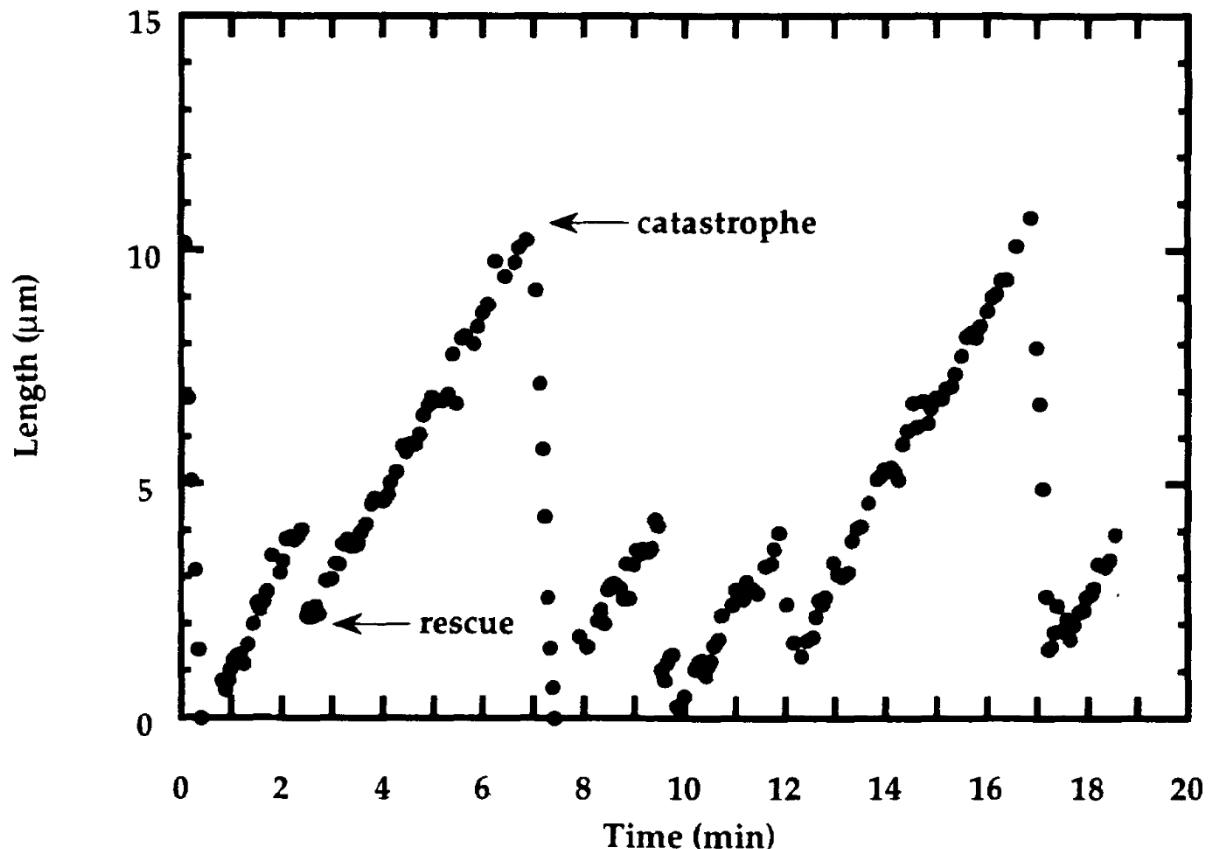
# Instabilité dynamique



# Instabilité dynamique



# Instabilité dynamique



# Instabilité dynamique

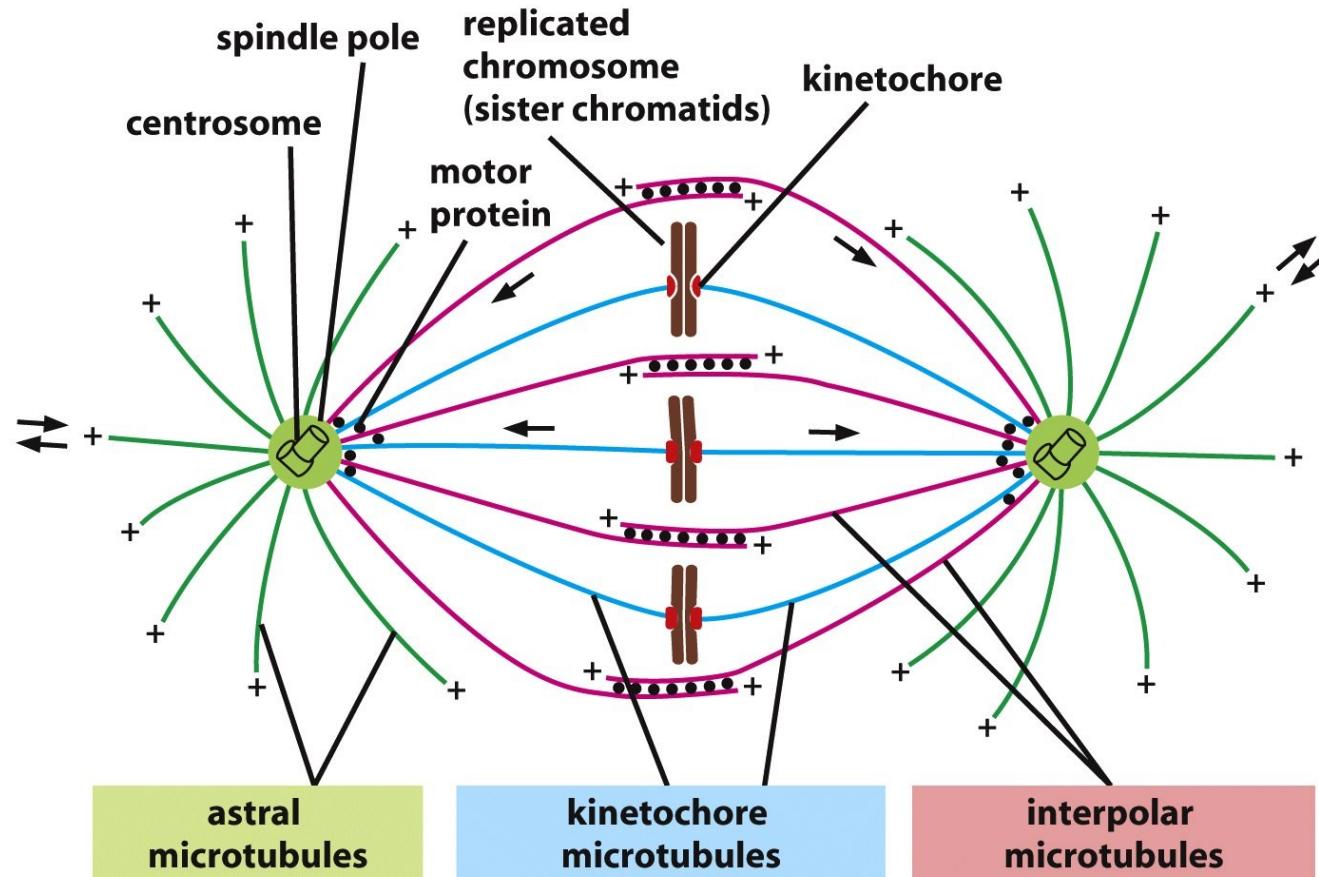
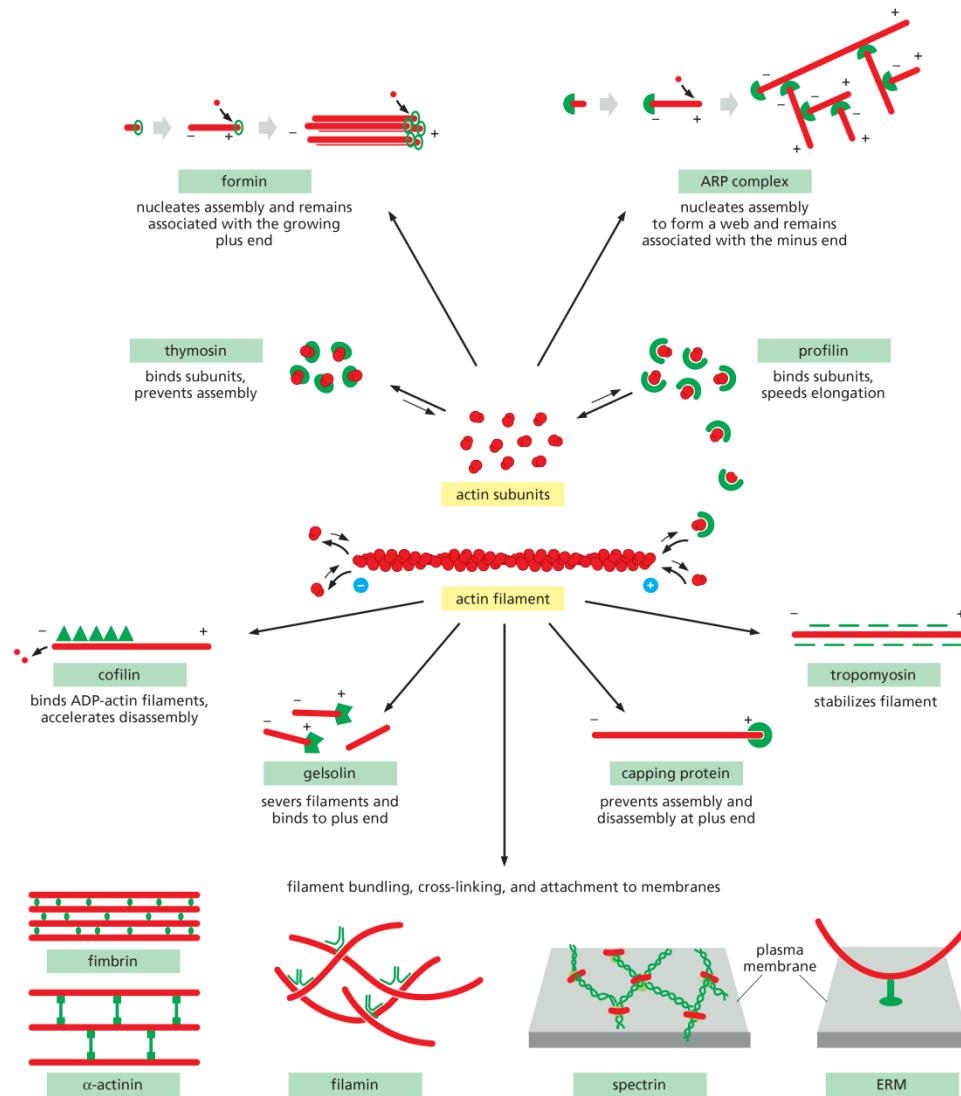
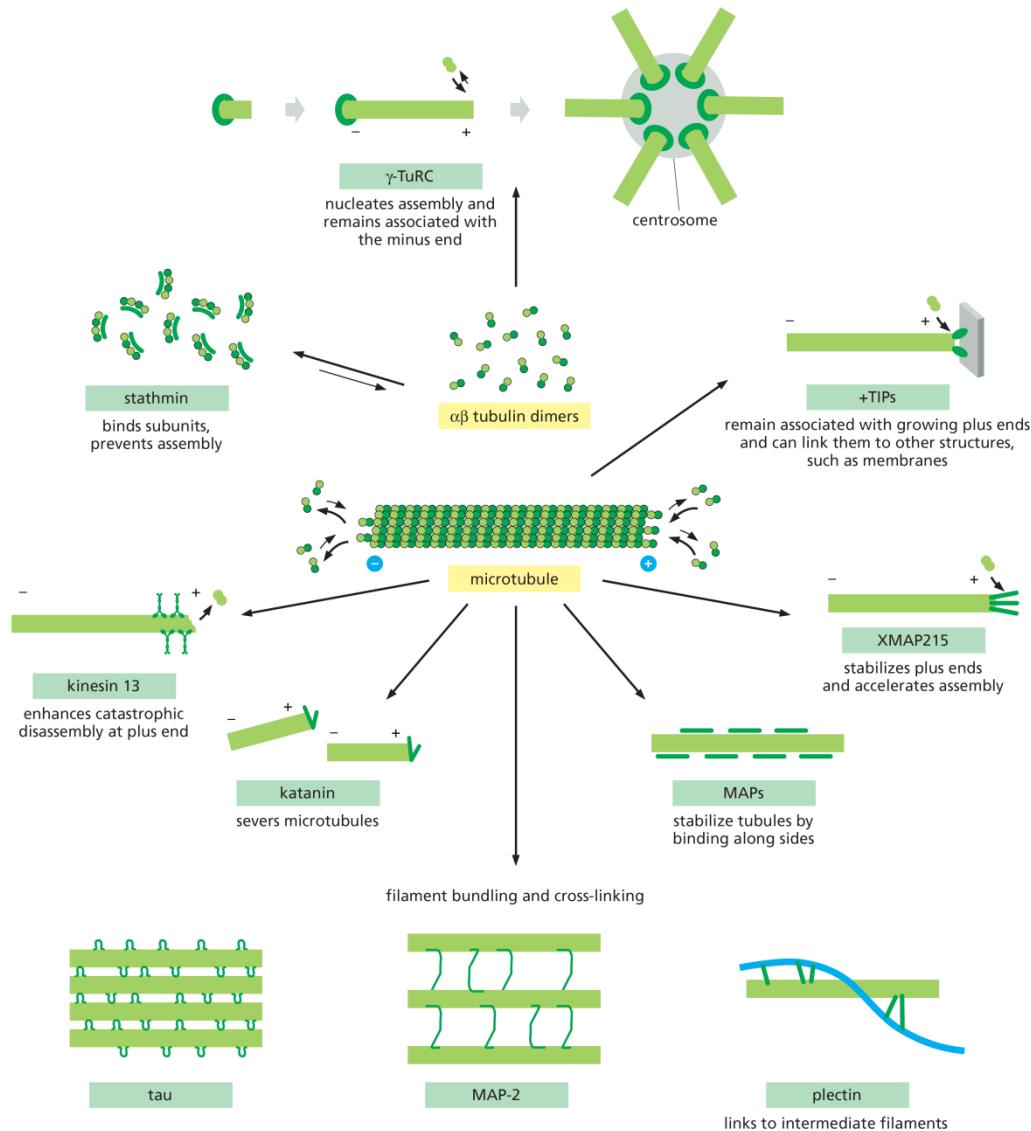


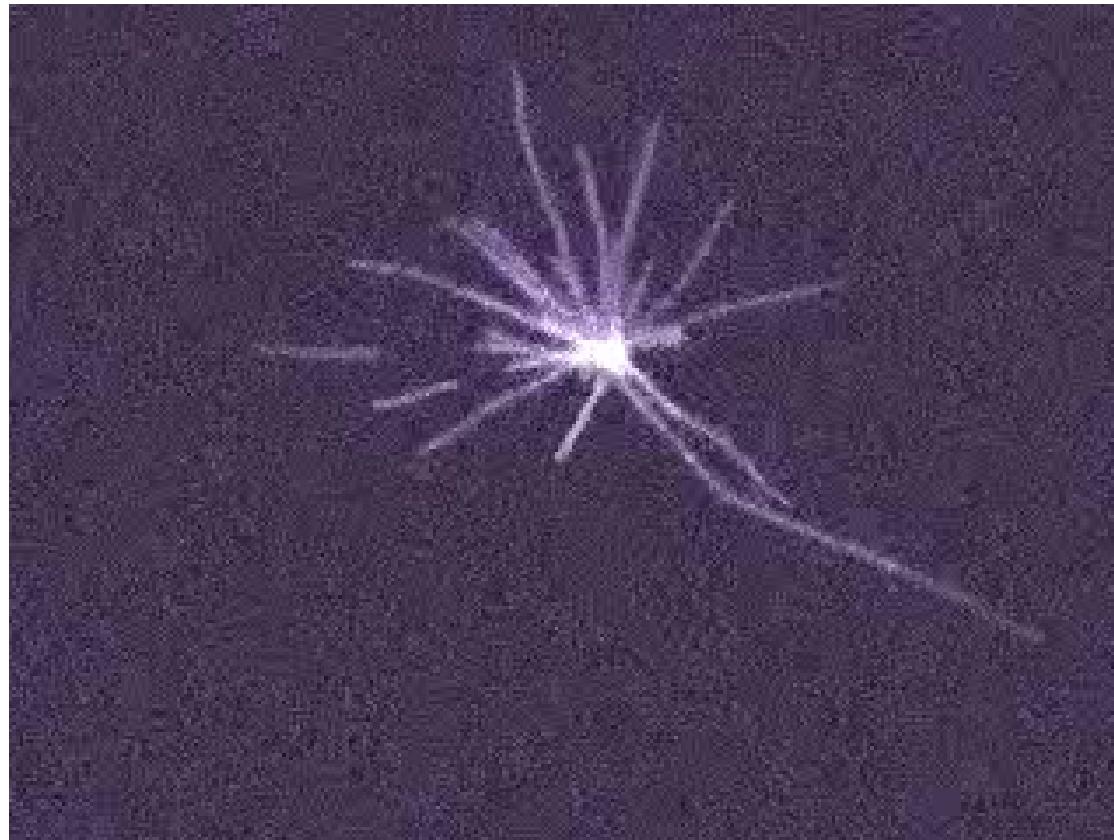
Figure 16-85a Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Les biopolymères

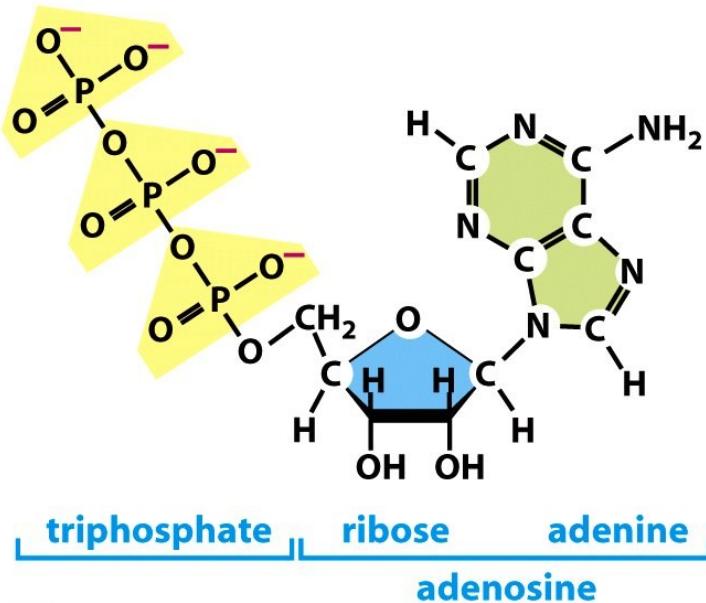




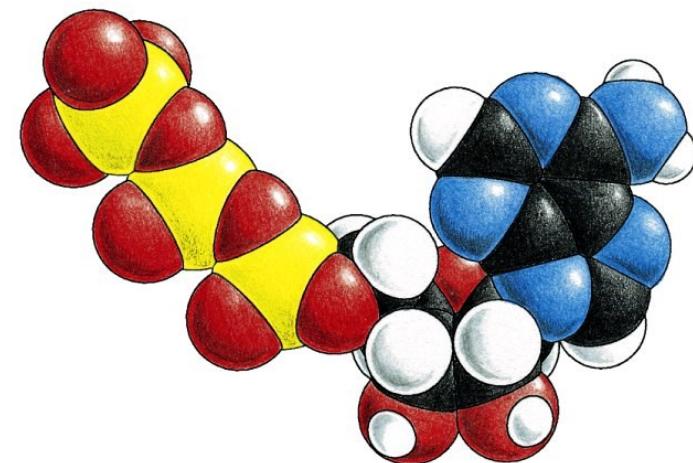
# Instabilité dynamique μtubules



# ATP



(A)



(B)

Figure 2-26 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# ATP

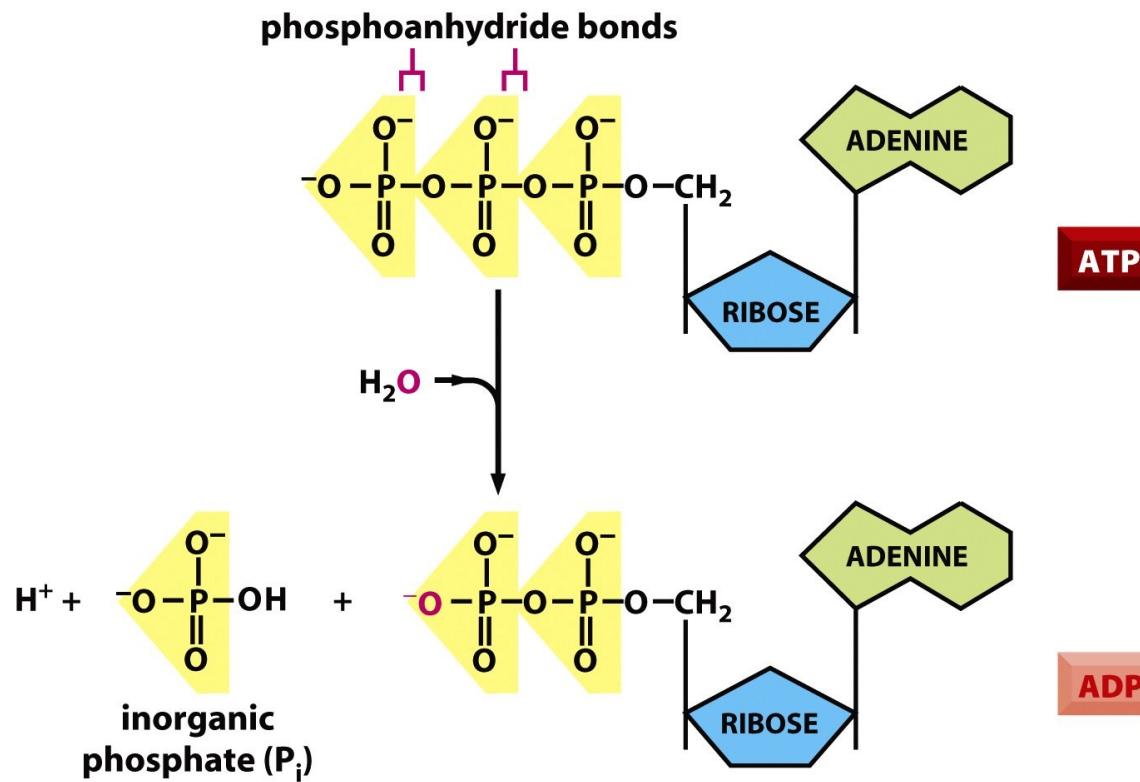


Figure 2-57 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires

- ATP Synthase
  - Se trouve dans la membrane des mitochondries
  - Production d'ATP soit 100 molécules par seconde
  - 8000 rpm



# Moteurs moléculaires

## ■ ATP Synthase

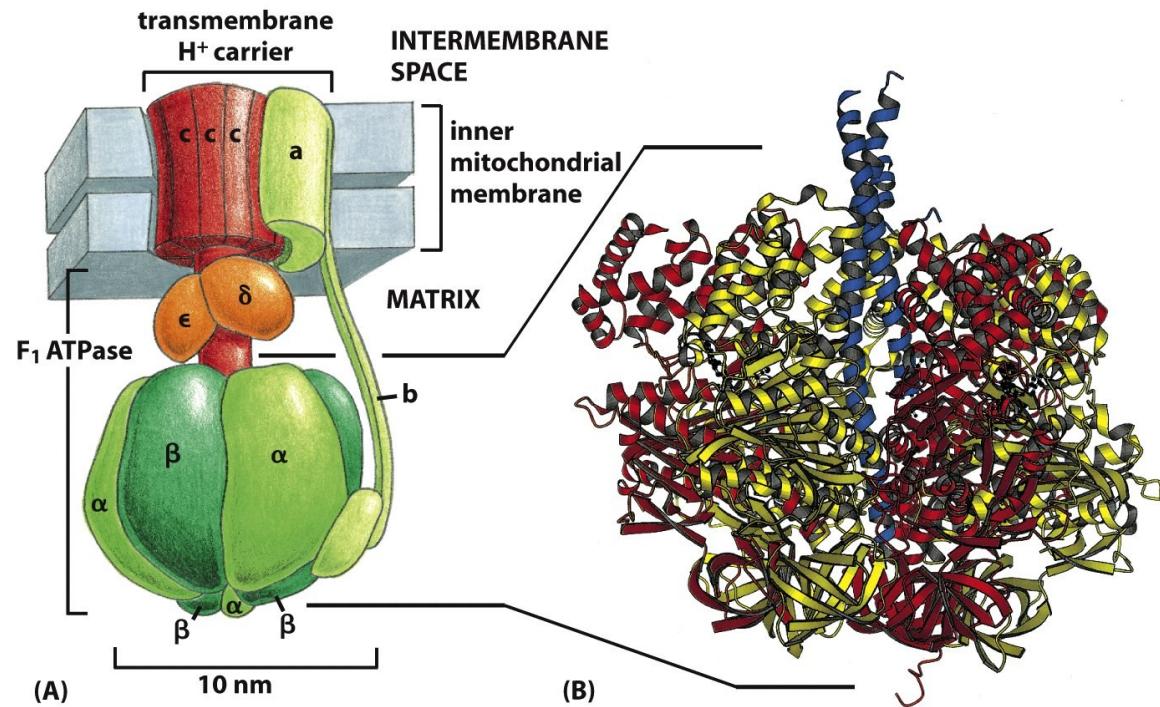


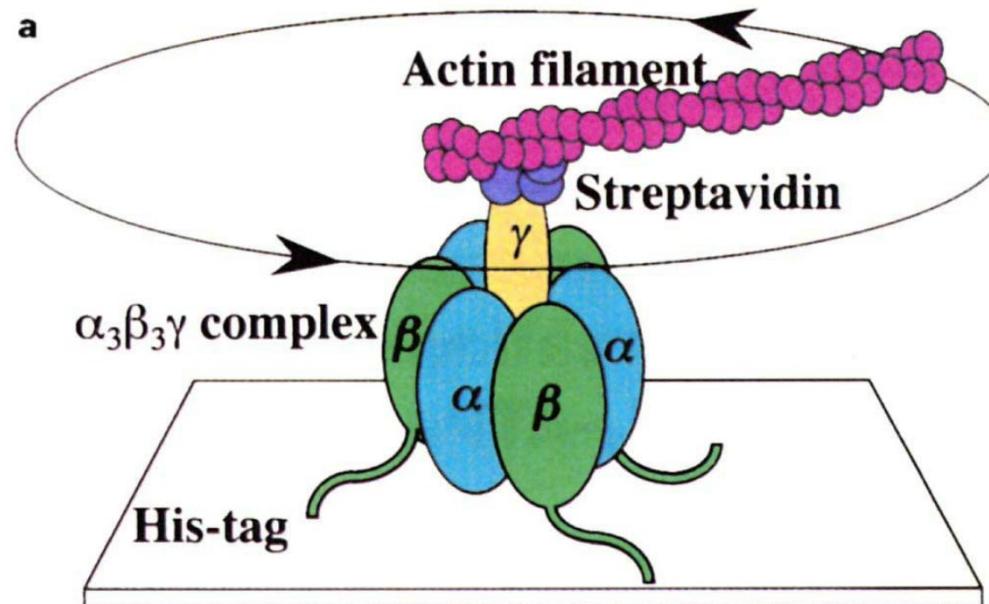
Figure 14-15 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires

- ATP Synthase

# Moteurs moléculaires

- ATP Synthase



Coverslip coated with Ni-NTA

# Moteurs moléculaires

- Myosin II :
  - S'accroche à l'actine

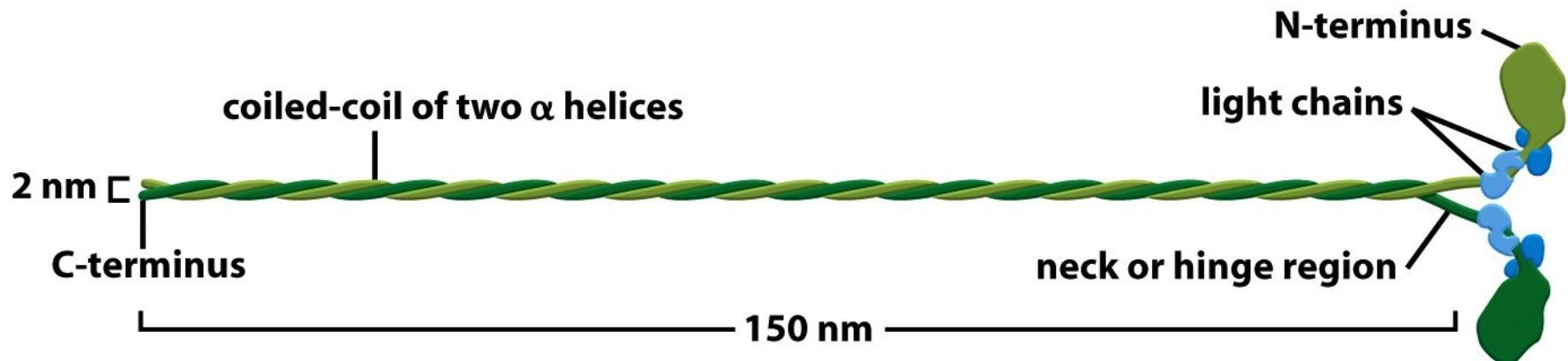


Figure 16-54a Molecular Biology of the Cell 5/e (© Garland Science 2008)

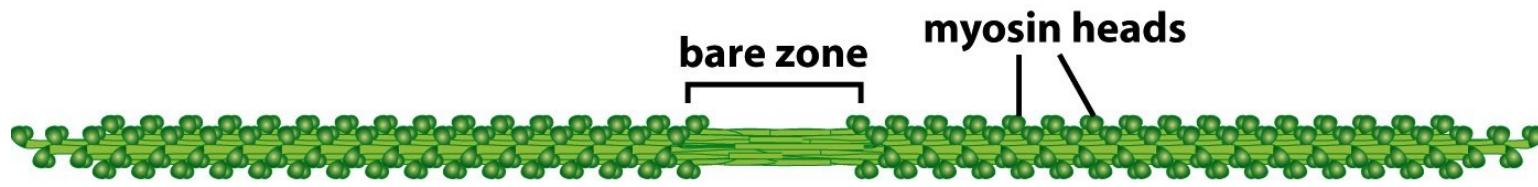
# Moteurs moléculaires

- Myosin II :



(A)

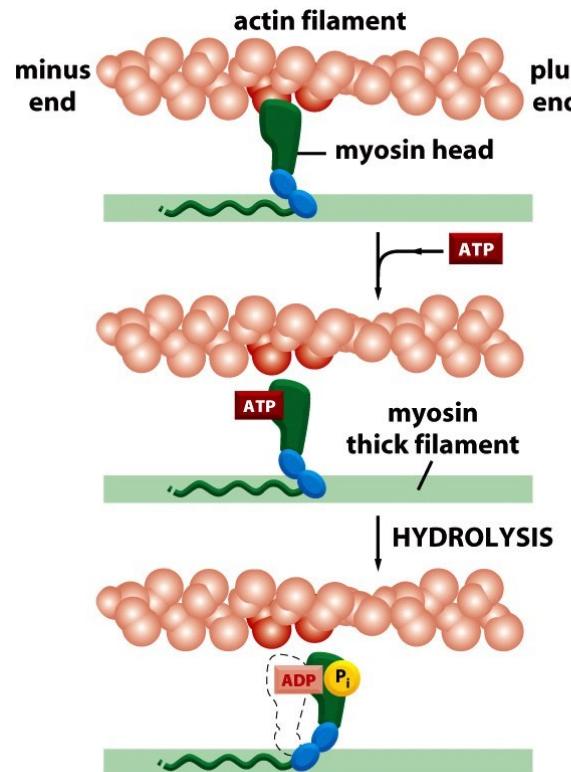
500 nm



(B)

Figure 16-55ab Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires



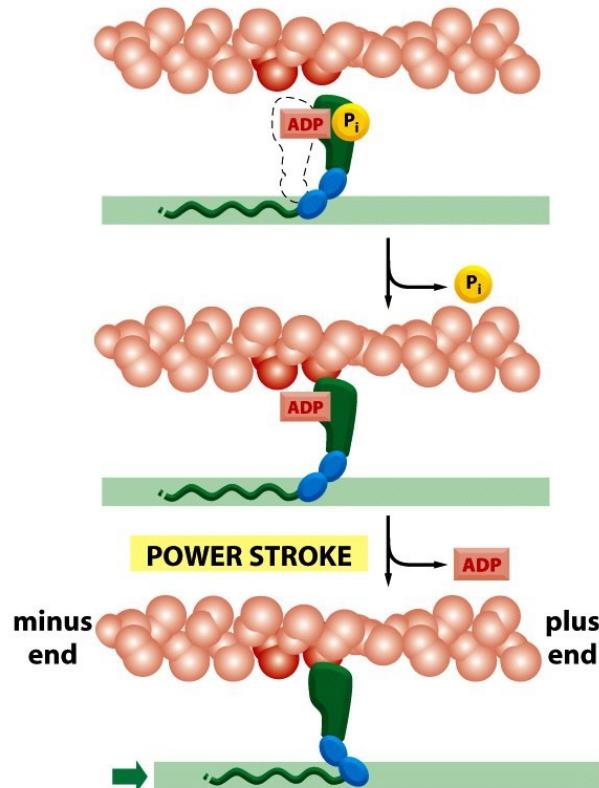
**ATTACHED** At the start of the cycle shown in this figure, a myosin head lacking a bound nucleotide is locked tightly onto an actin filament in a *rigor* configuration (so named because it is responsible for *rigor mortis*, the rigidity of death). In an actively contracting muscle, this state is very short-lived, being rapidly terminated by the binding of a molecule of ATP.

**RELEASED** A molecule of ATP binds to the large cleft on the “back” of the head (that is, on the side furthest from the actin filament) and immediately causes a slight change in the conformation of the domains that make up the actin-binding site. This reduces the affinity of the head for actin and allows it to move along the filament. (The space drawn here between the head and actin emphasizes this change, although in reality the head probably remains very close to the actin.)

**COCKED** The cleft closes like a clam shell around the ATP molecule, triggering a large shape change that causes the head to be displaced along the filament by a distance of about 5 nm. Hydrolysis of ATP occurs, but the ADP and inorganic phosphate ( $P_i$ ) produced remain tightly bound to the protein.

Figure 16-61 part 1 of 2 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires



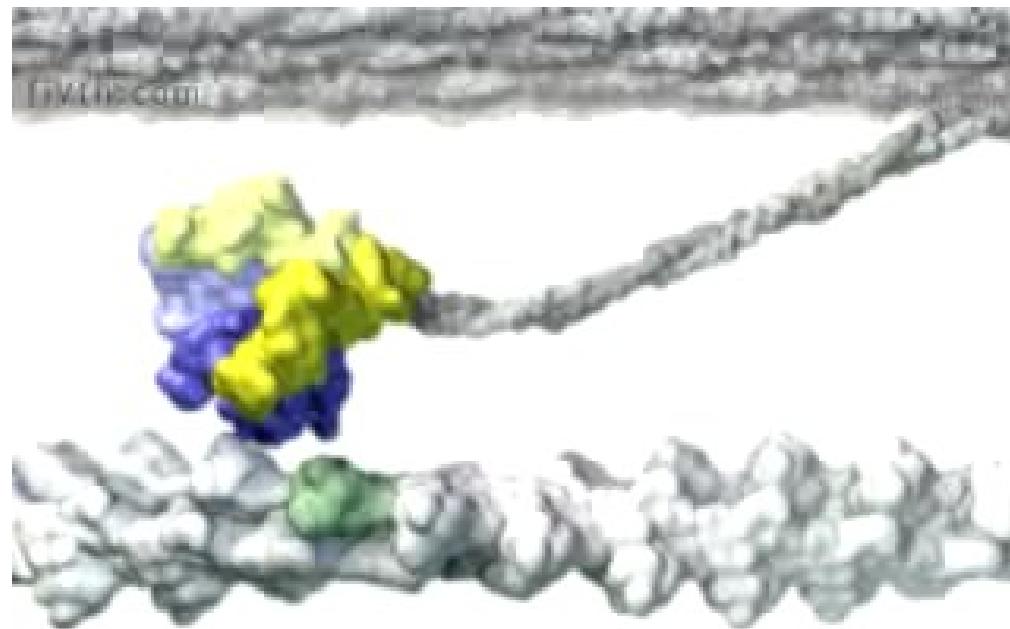
**COCKED** The cleft closes like a clam shell around the ATP molecule, triggering a large shape change that causes the head to be displaced along the filament by a distance of about 5 nm. Hydrolysis of ATP occurs, but the ADP and inorganic phosphate ( $P_i$ ) produced remain tightly bound to the protein.

**FORCE-GENERATING** A weak binding of the myosin head to a new site on the actin filament causes release of the inorganic phosphate produced by ATP hydrolysis, concomitantly with the tight binding of the head to actin. This release triggers the power stroke—the force-generating change in shape during which the head regains its original conformation. In the course of the power stroke, the head loses its bound ADP, thereby returning to the start of a new cycle.

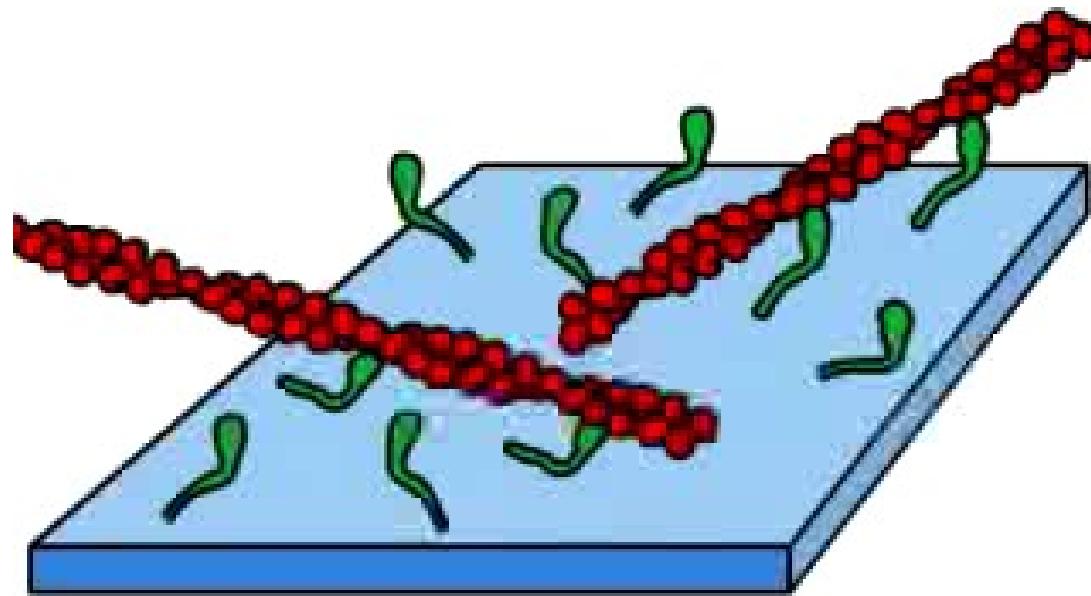
**ATTACHED** At the end of the cycle, the myosin head is again locked tightly to the actin filament in a rigor configuration. Note that the head has moved to a new position on the actin filament.

Figure 16-61 part 2 of 2 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires



# Moteurs moléculaires



# Moteurs moléculaires

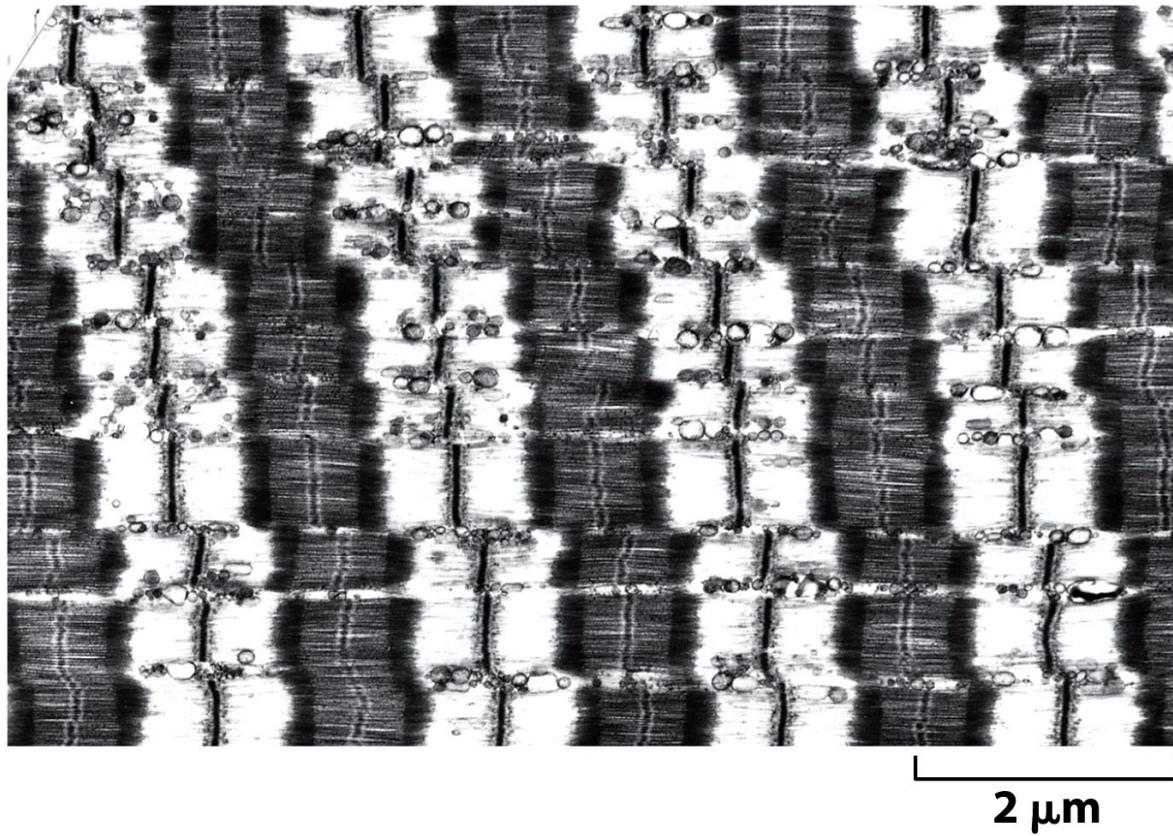


Figure 16-74a Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires

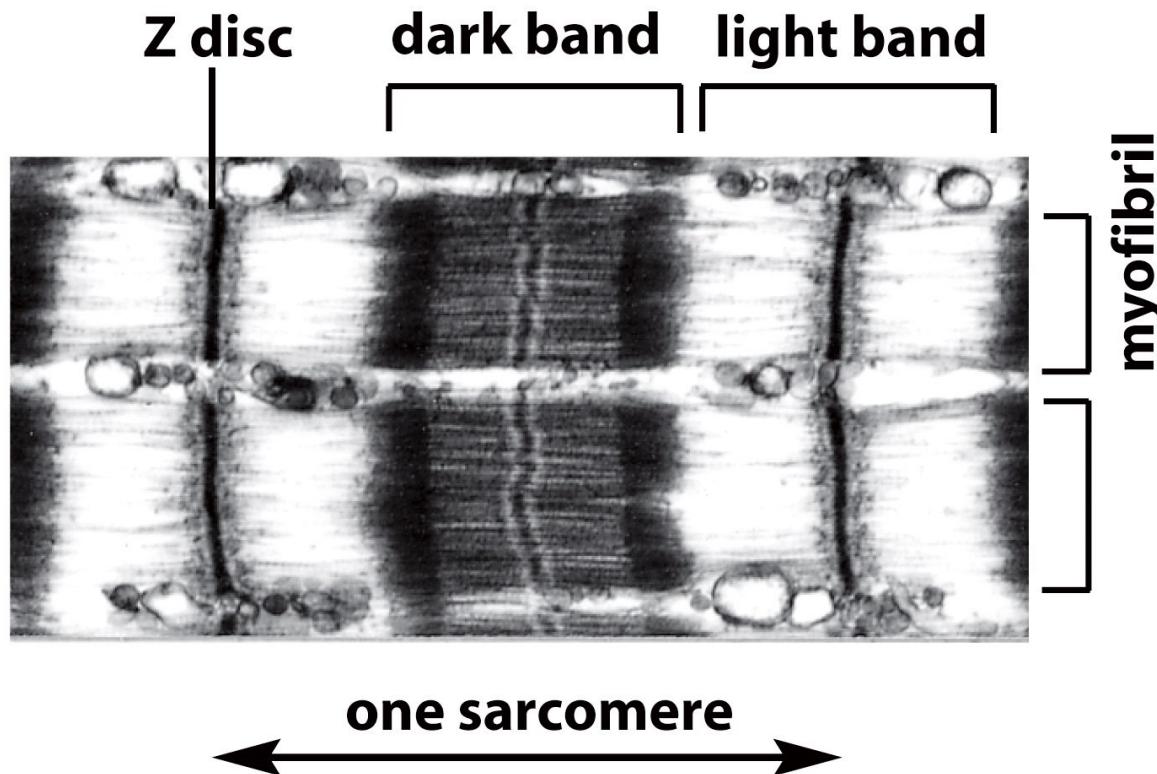
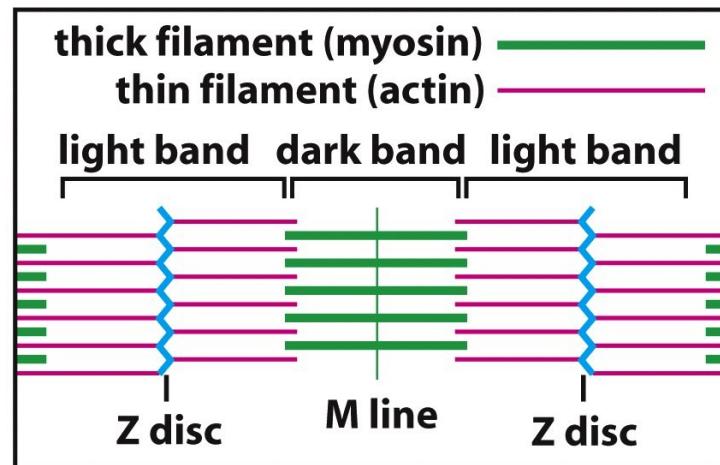
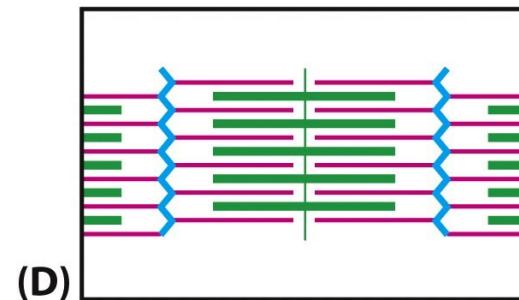


Figure 16-74b Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Moteurs moléculaires



(C)

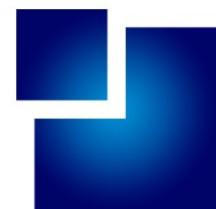


(D)

Figure 16-74cd Molecular Biology of the Cell 5/e (© Garland Science 2008)

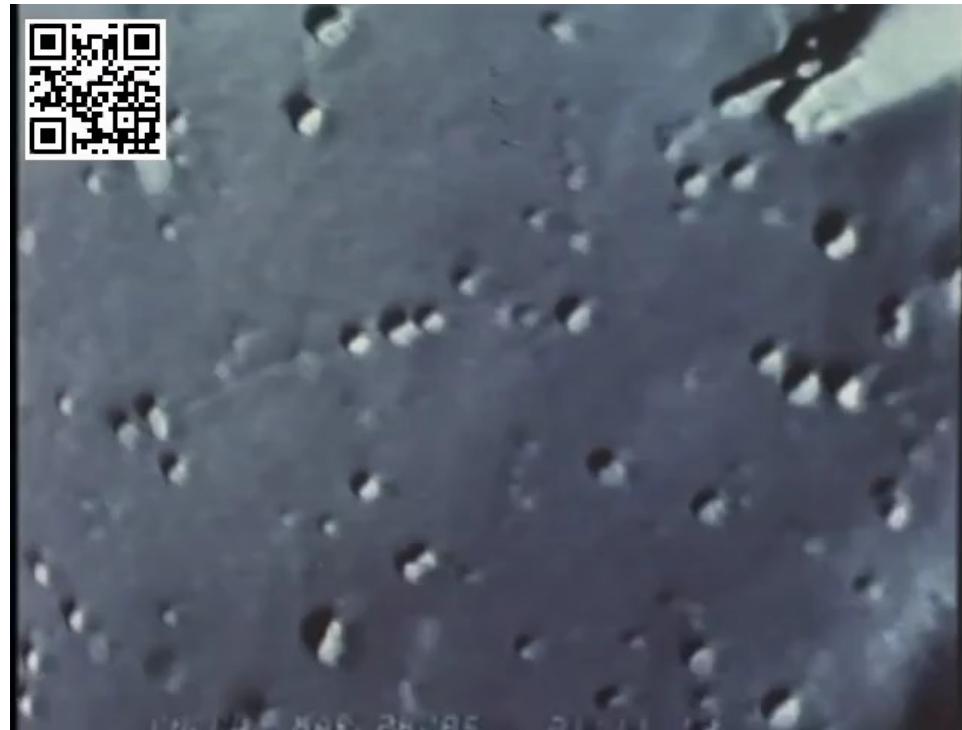
# Moteurs moléculaires

- Kinesin



# Moteurs moléculaires

- Kinesin



# Moteurs moléculaires

## ■ Kinesin

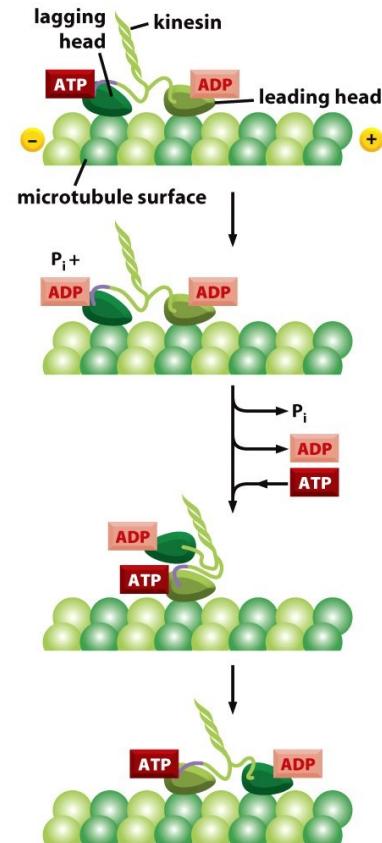
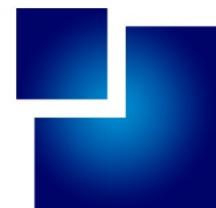
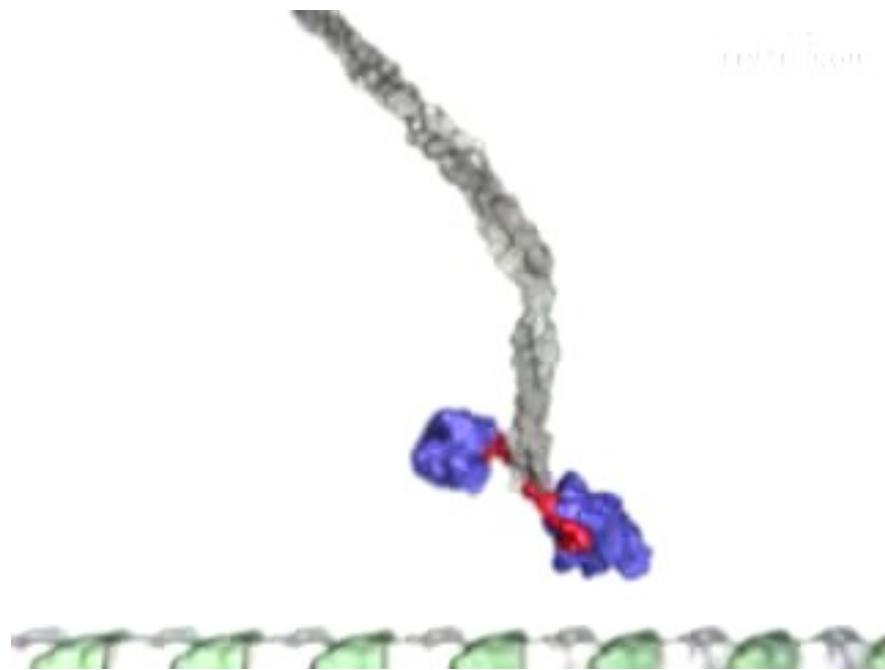


Figure 16-62 Molecular Biology of the Cell 5/e (© Garland Science 2008)

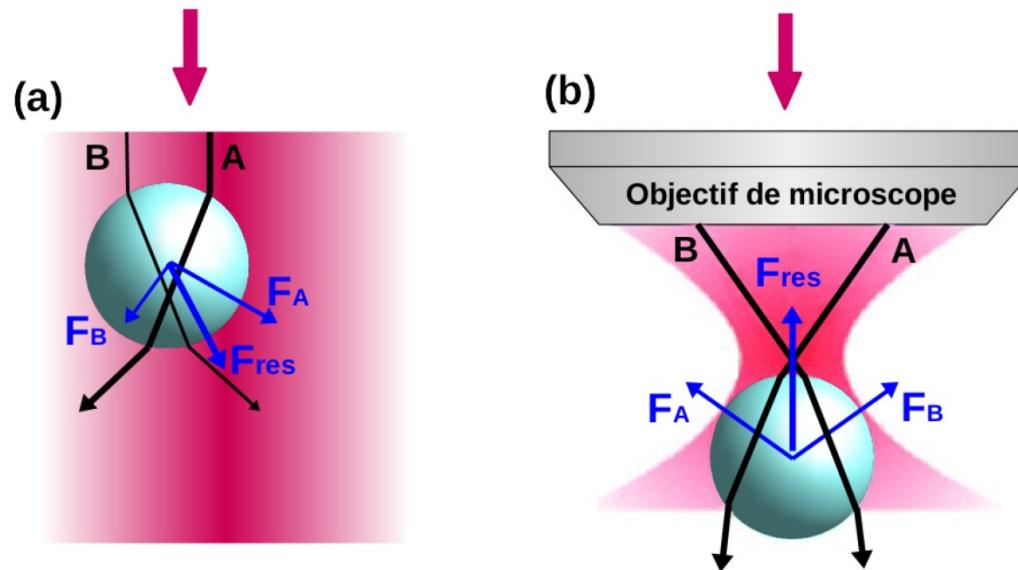
# Moteurs moléculaires

- Kinesin



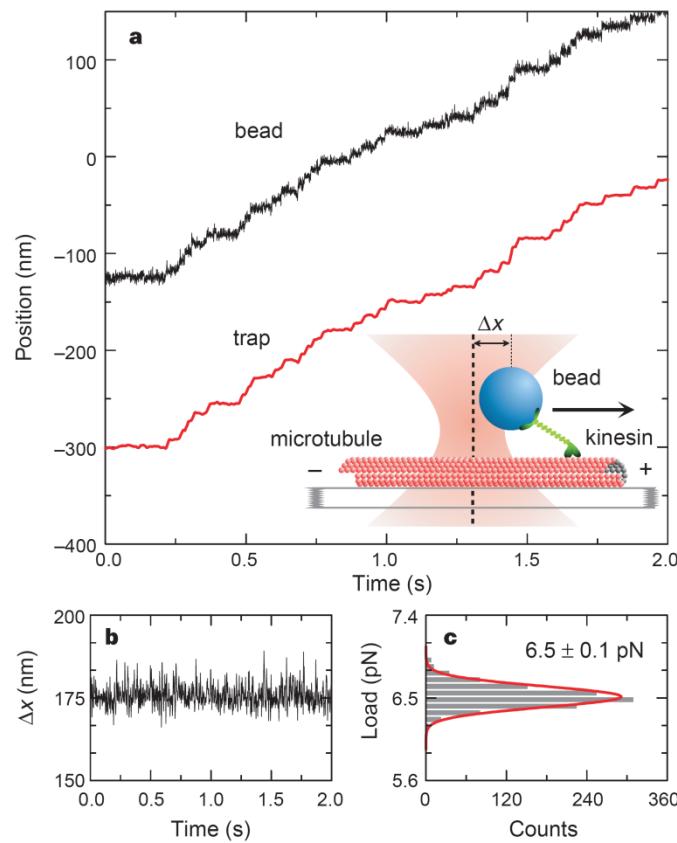
# Moteurs moléculaires

- Pince optique



# Moteurs moléculaires

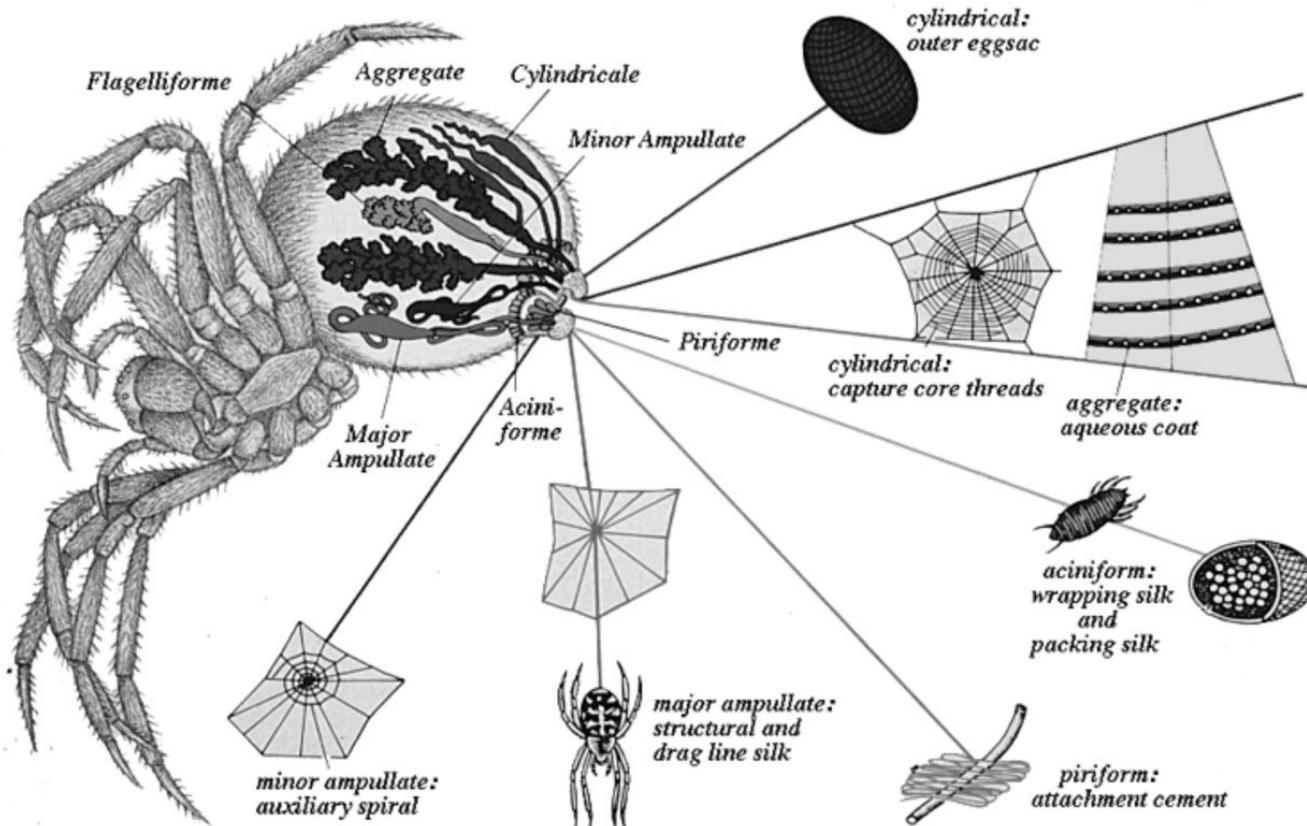
- Kinesin



# Soie d'araignée

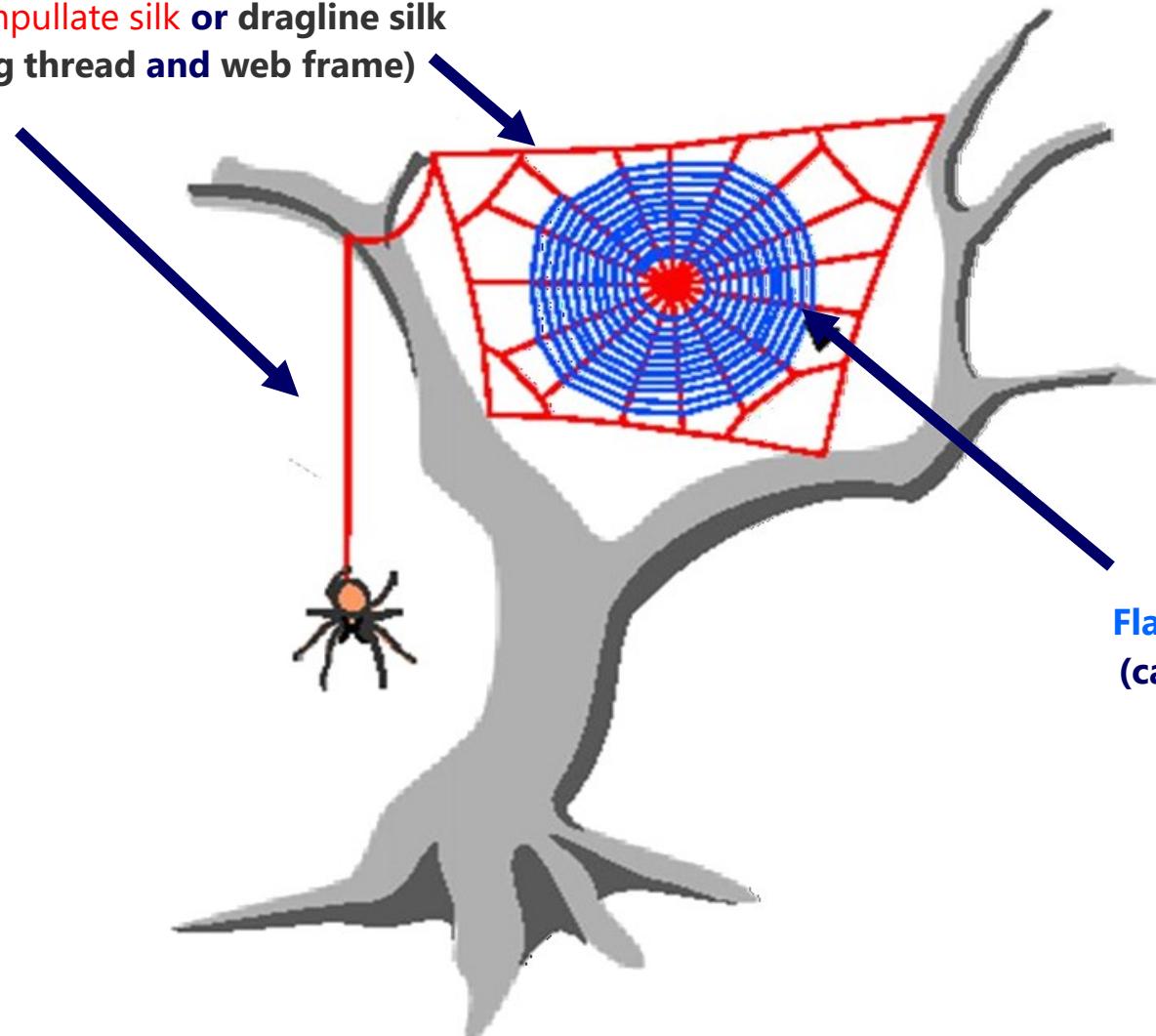


# Soie d'araignée



major ampullate silk **or** dragline silk  
(roping thread and web frame)

Flagelliform silk  
(capture spiral)



# Soie d'araignée vs le monde

	Density [g.cm <sup>-3</sup> ]	Strength [GPa]	Extensibility [%]	Thoughness MJ.m <sup>-3</sup>
Nylon	1,1	0,950	18	80
Kevlar	1,4	3,600	2,7	50
Dragline silk	1,3	1,100	30	160
Flagelliform silk	~1,3	0,500	270	150
Elastin	~1,1	0,002	150	2

Gosline, Guerette, Ortlepp and Savage, *J Exp. Bio.*  
1999, 3295-3303

# Fabrication

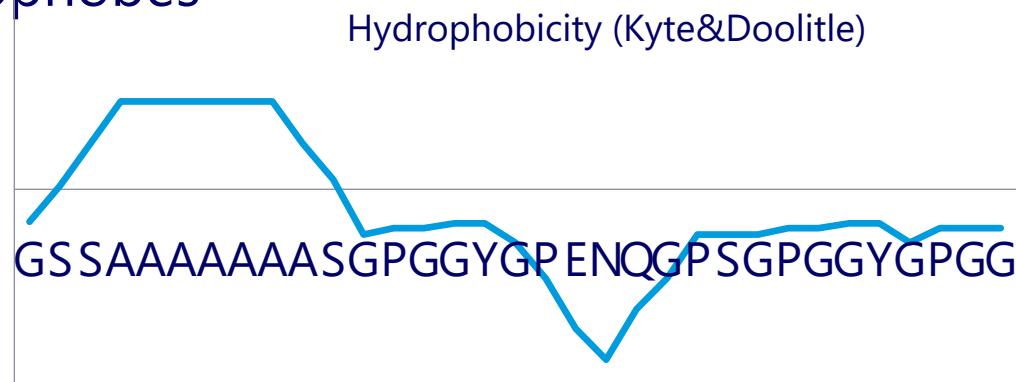
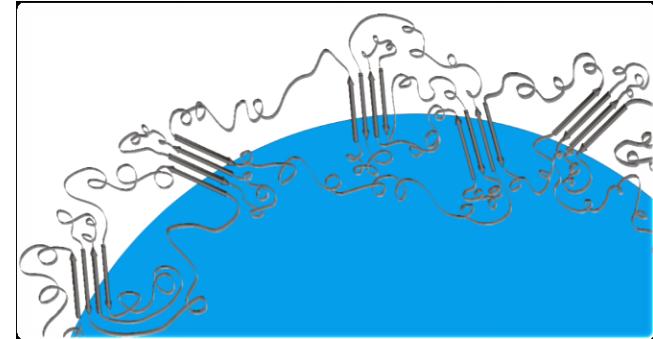
Elevage d'araignée : pas possible

Dévidage possible : long et coûteux

Production bactérienne

# Propriétés interfaciales

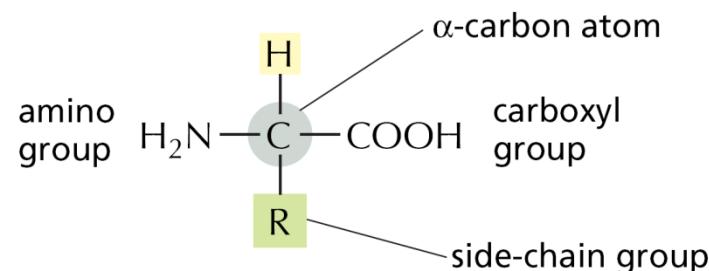
- Soie d'araignée:
  - amphiphile
  - Séquence qui se répètent
  - Très bonne séparation des parties hydrophiles et hydrophobes



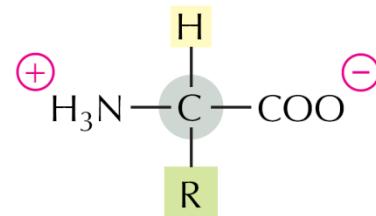
# Structure des protéines

## THE AMINO ACID

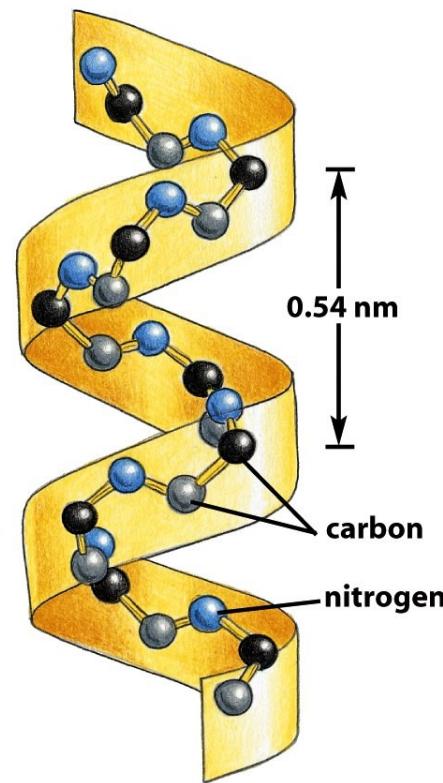
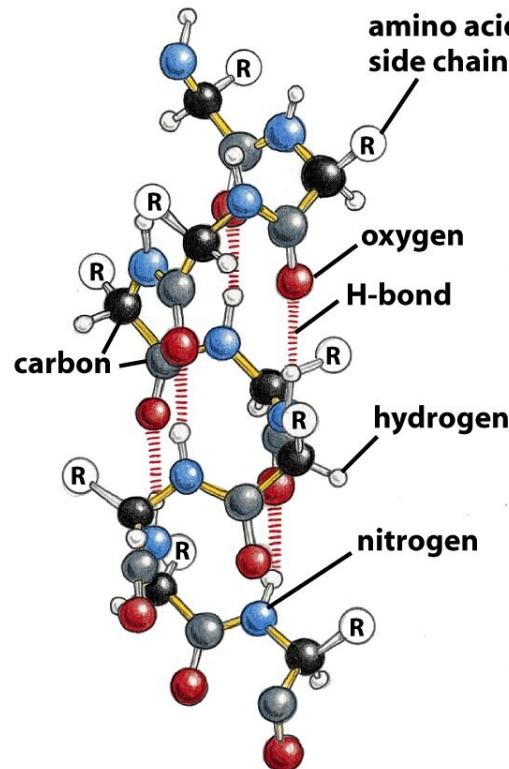
The general formula of an amino acid is



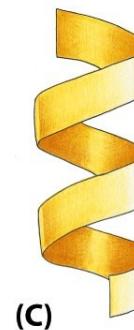
$R$  is commonly one of 20 different side chains.  
At pH 7 both the amino and carboxyl groups  
are ionized.



# Structure des protéines



$\alpha$  helix



(A)

(B)

Figure 3-7a-c Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Structure des protéines

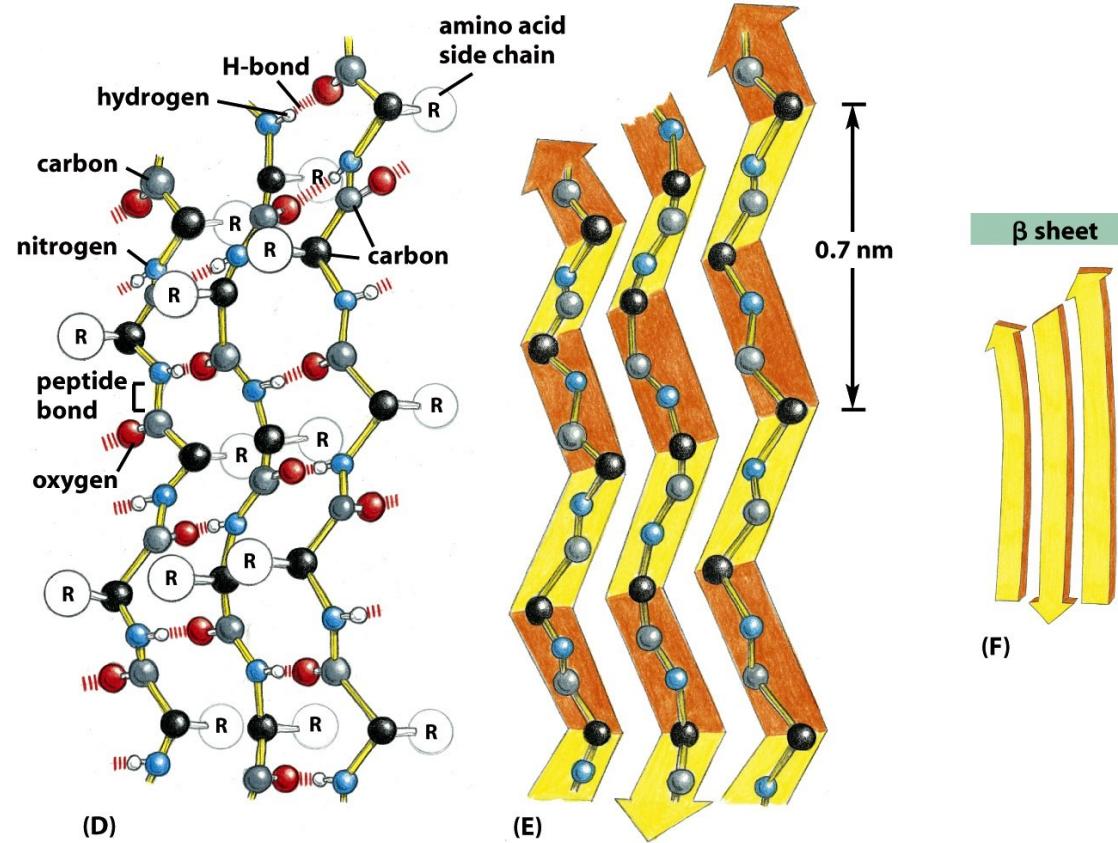


Figure 3-7d-f Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Structure des protéines

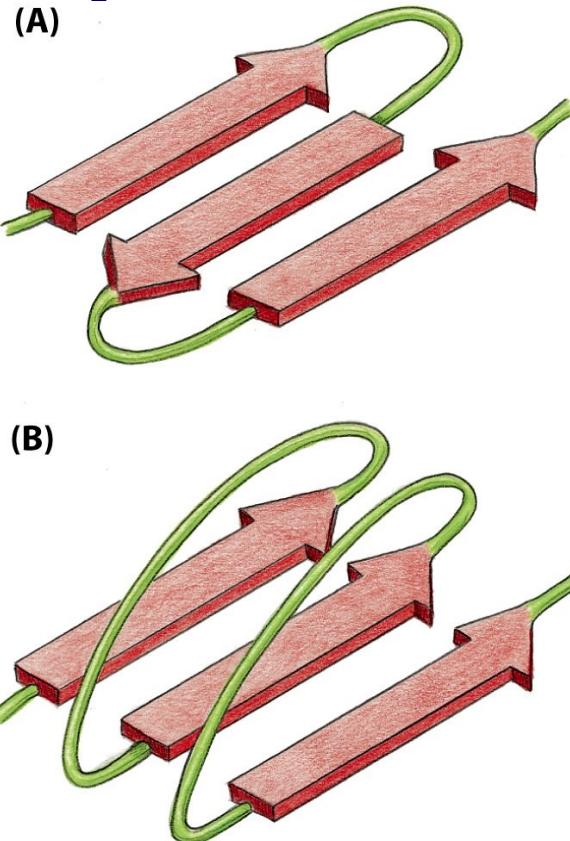
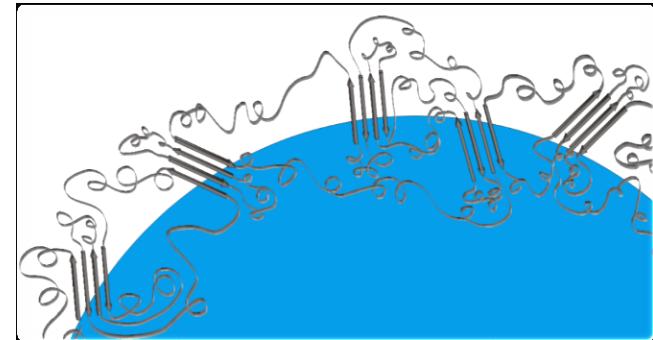


Figure 3-8 Molecular Biology of the Cell 5/e (© Garland Science 2008)

# Structure secondaire

- FTIR pour la mesure de la structure secondaire (Fourier Transform Infrared Spectroscopy)

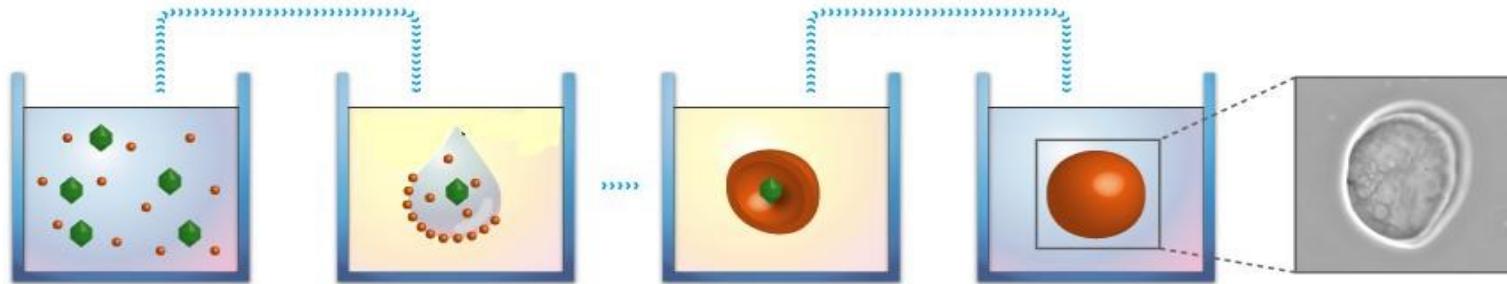


	$\alpha$ -helix	$\beta$ -sheet	$\beta$ -turn	Random coil
C16	19	35	32	13,8

U. Slotta, M. Tammer, F. Kremer, P. Koelsch, T. Scheibel  
*Supramolecular Chemistry*, 2006, **5**, 465

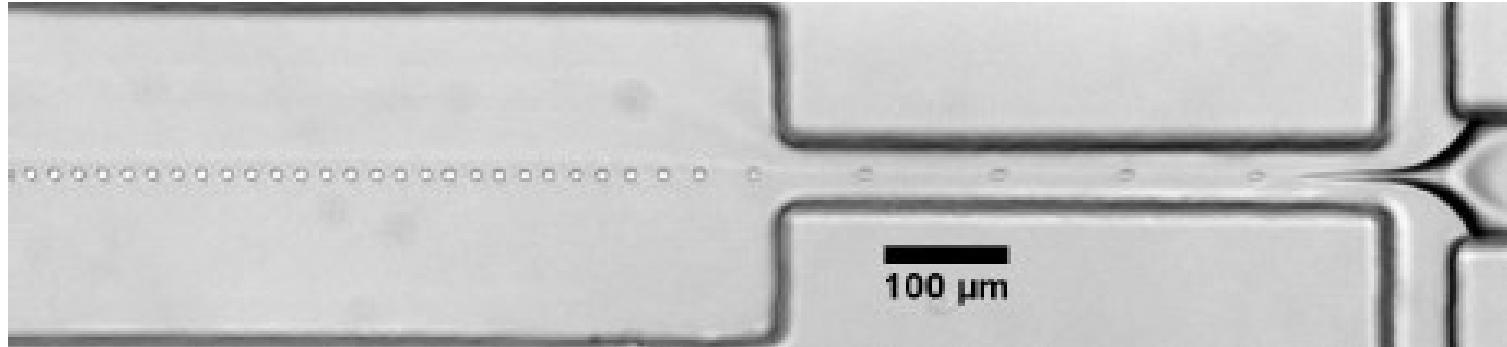
# Fabrication de capsules

- Emulsion



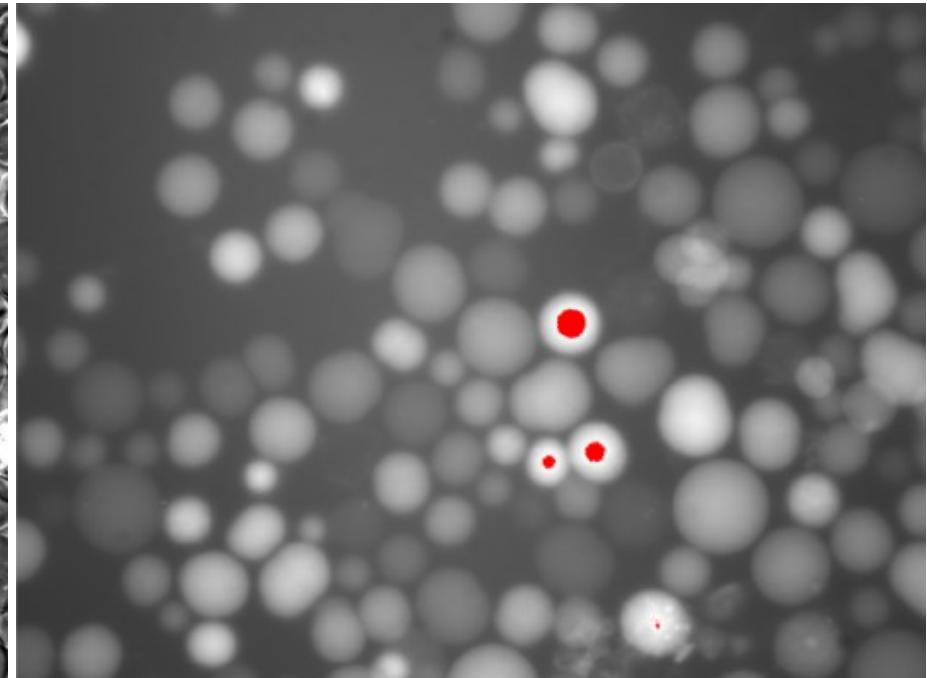
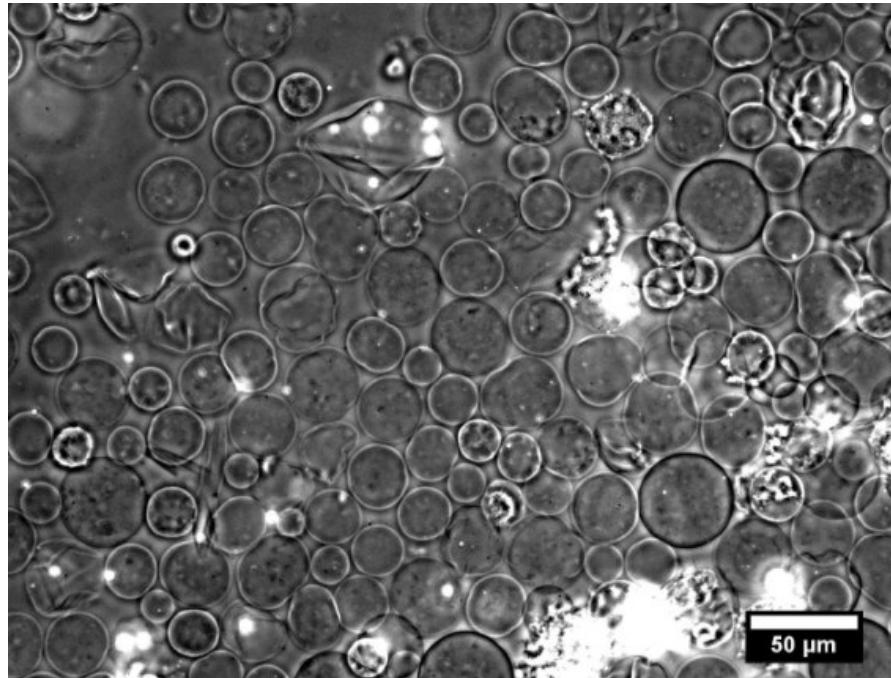
Hermanson *et al*, Advanced Materials, 19(14)

- Microfluidique

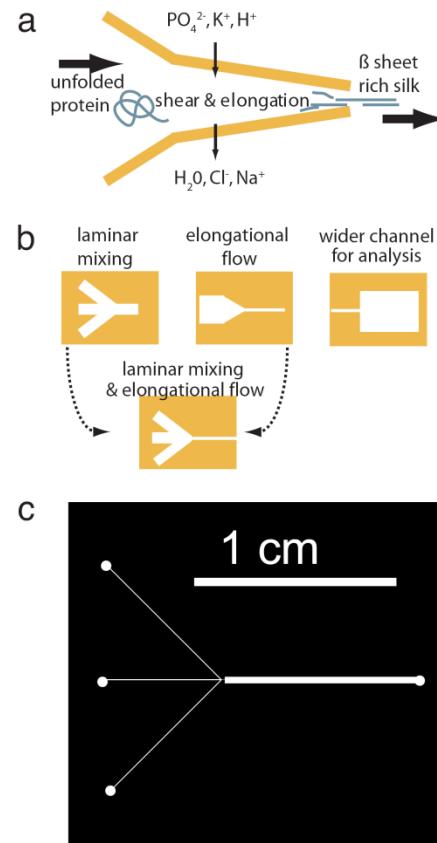


Markus Harasim, TUM

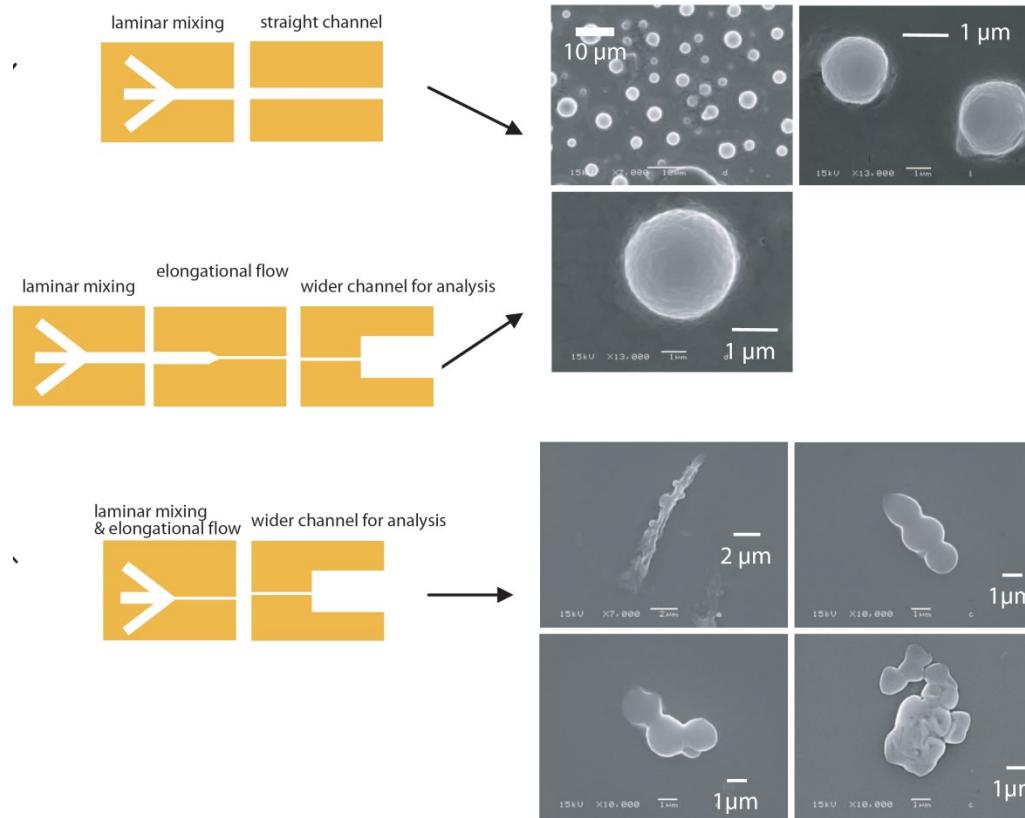
# Fabrication de capsules



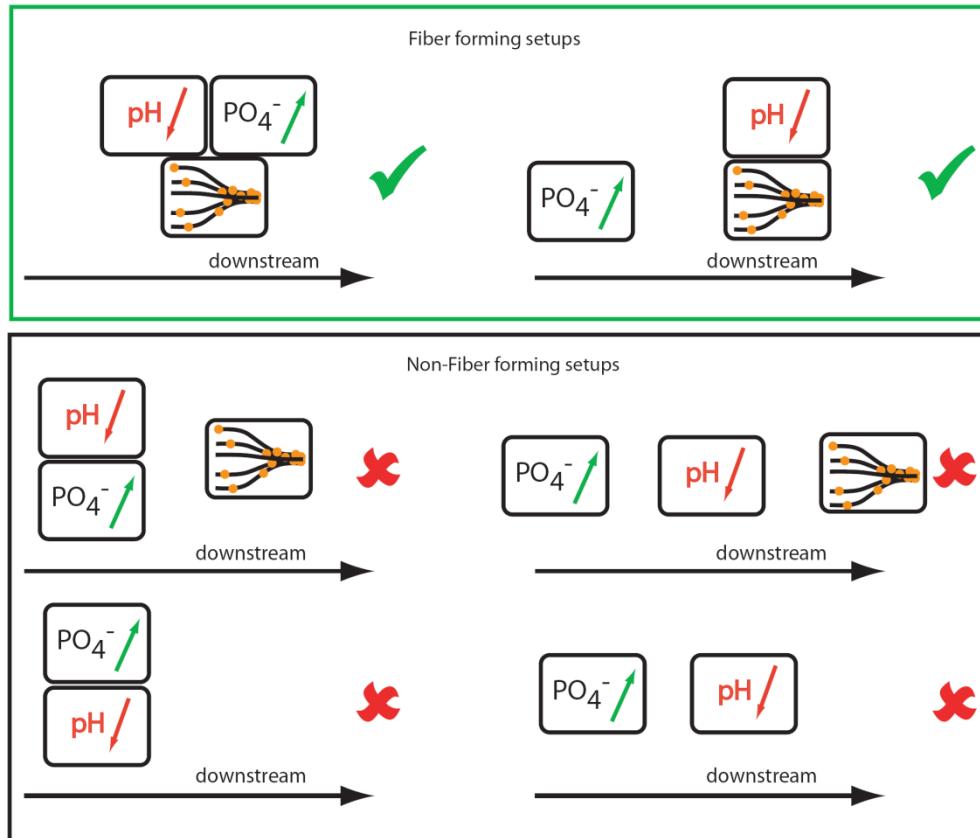
# Fabrication d'une fibre



## Fabrication d'une fibre



## Fabrication d'une fibre



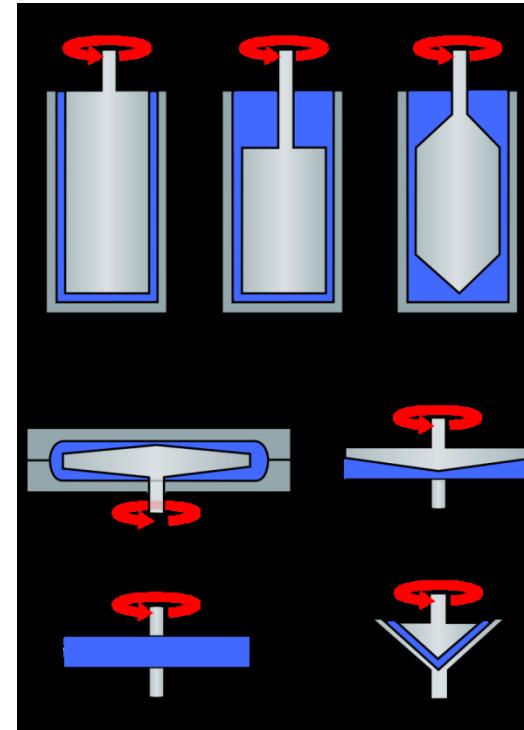
# Rhéologie



# Rhéologie

On applique une contrainte, un cisaillement

On mesure la déformation qui en résulte



# Rhéologie

Pour une sollicitation en cisaillement on peut écrire :

$$G^* = \frac{\sigma}{\epsilon}$$
$$G^* = G' + iG''$$

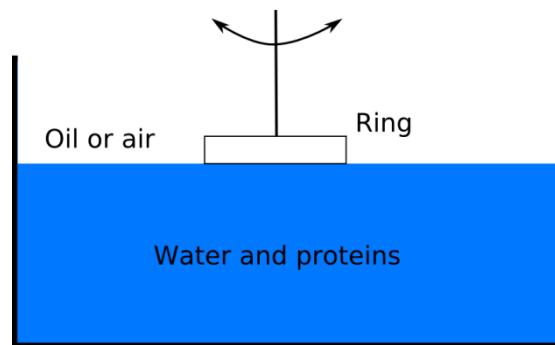
avec  $\sigma$  la contrainte et  $\epsilon$  la déformation

$G'$  décrit le comportement élastique

$G''$  décrit le comportement visqueux

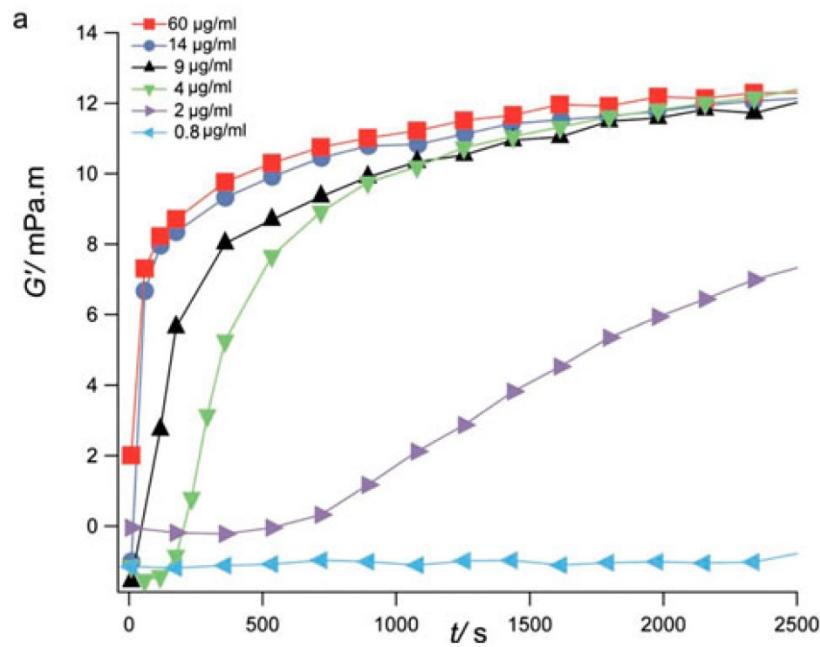
# Rhéologie interfaciale

- Adsorption et propriétés mécaniques



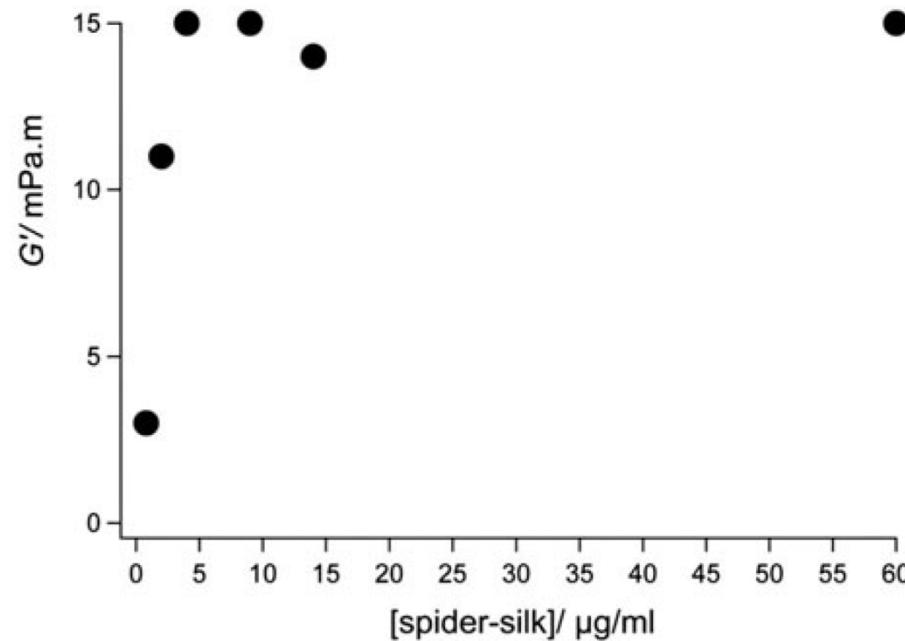
- Du Noüy Ring ( 40 mm,  $e=0,46\text{mm}$ )

# Rhéologie interfaciale

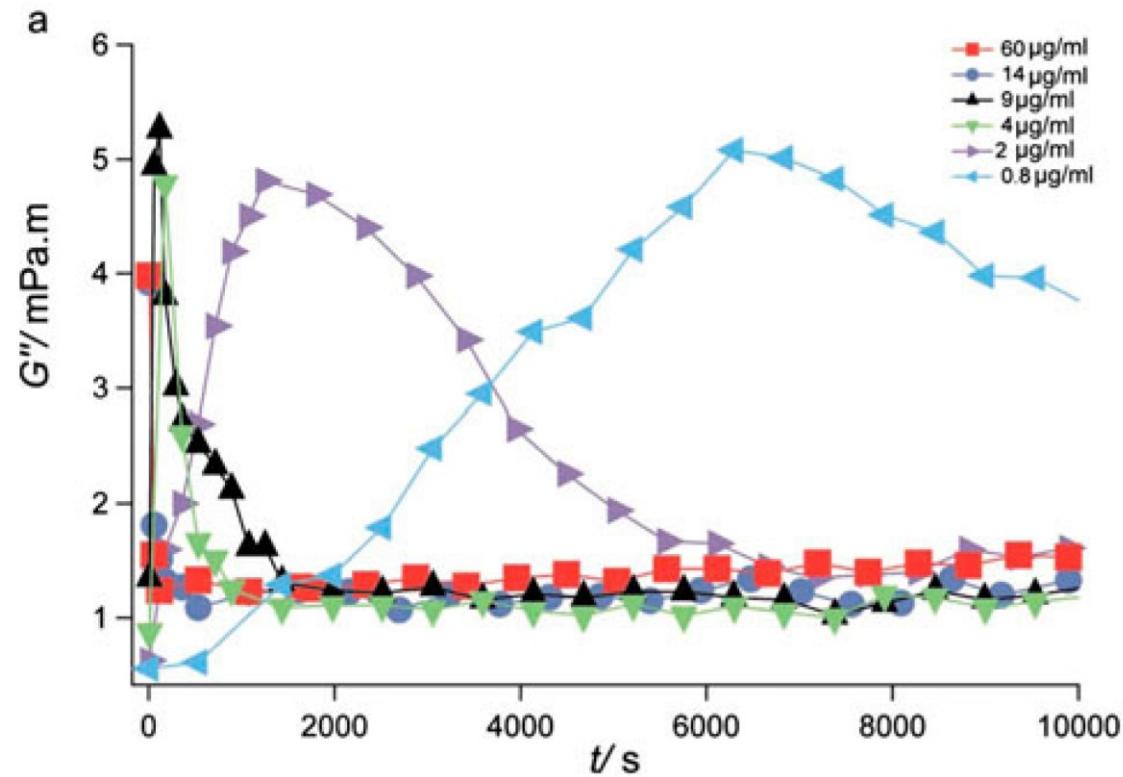


# Rhéologie interfaciale

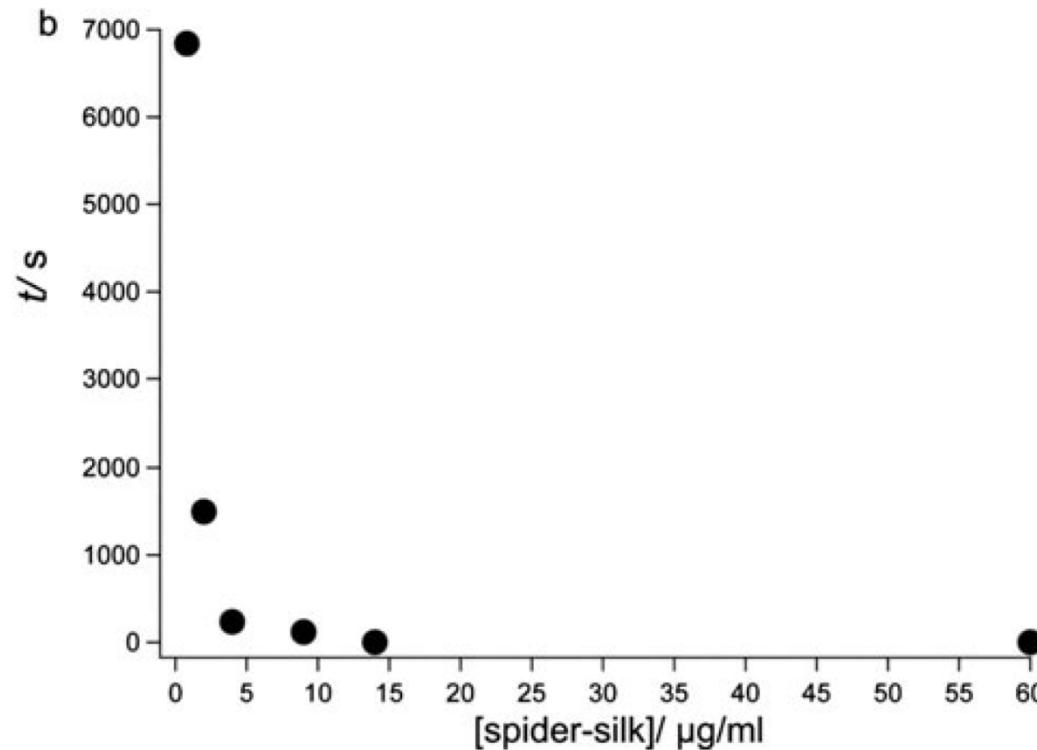
b



# Rhéologie interfaciale



# Rhéologie interfaciale



# Modification du film interfacial

- Ajout de phosphate

	$\alpha$ -helix	$\beta$ -sheet	$\beta$ -turn	Random coil
C16	19	35	32	13,8
C16+phosphate	13,2	52,1	25,5	9,2

Augmentation  $\beta$ -sheet

Interconnexion et renforcement

Ajustement des propriétés mécaniques du film

# Modification du film interfacial

