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WORKSHOP ON:
PROTEINS, MEMBRANES and their INTERACTIONS

22 JULY - 2 AUGUST 1996

"Microscopic determination of the elastic constants of amphiphilic layers"

PART III

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Molecular Theory of Curvature Elasticity in Surfactant Films

Theory of chain packing.

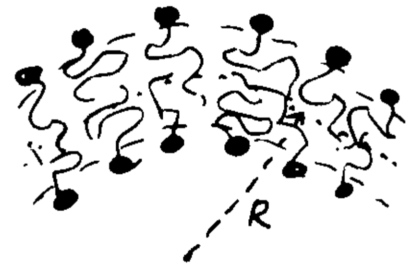
Derivation of elastic constants expressions from theory of chain packing.

Typical results: variation of elastic constants with chain length, average area per molecule and composition (in mixed aggregates). Stability of planar bilayers in mixed and pure aggregates.

Helfrich's free energy:

$$\frac{f}{a} = \frac{1}{2} k (c_1 + c_2 - c_0)^2 + \bar{k} c_1 c_2 \; ; \; c_1 = \frac{1}{R_1} , c_2 = \frac{1}{R_2}$$

constant area!! 2-D Hamiltonion



k = bending constant

$\bar{k}$ = saddle-splay const

c_0 = spontaneous curvat

Layers are not 2-D so define area at surface of inextension!!

Is it possible to keep a constant?

More general approach:

Expand the free energy per molecule and find a that minimizes the free energy.

Choice of reference state: free energy per molecule

(i) Spontaneous state of the film: expand free energy around a_e and c_e.

$$f(a,c) = f(a_e, c_e) + \frac{1}{2}\lambda_e (a-a_e)^2 + \frac{1}{2} k_e (c-c_e)^2 + \omega_e (a-a_e)(c-c_e)$$

λ_e, k_e, ω_e measure deviations from equilibrium state

$a_e \Rightarrow \frac{\partial f}{\partial a} = 0$; $c_e \Rightarrow \frac{\partial f}{\partial c} = 0$

From stability $\Rightarrow \lambda_e k_e > \omega_e^2$

area and curvature can be measured anywhere.

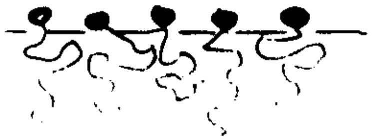
we can eliminate the cross term by imposing

$$\left(\frac{\partial^2 f}{\partial a \partial c}\right)_{a=a_e;\, c=c_e} = 0$$

and this will define the 'surface of inextension'; then a and c have to be measured there

(ii) Expansion for a tensionless flat surface.

$$\left(\frac{\partial f}{\partial a}\right)_{c=0} = 0 \quad ; \quad \left(\frac{\partial f}{\partial c}\right)_{c=0} = -k_f c_f \neq 0$$



$$f(a,c) = f(a_f, 0) - k_f c_f c + \frac{1}{2}\lambda_f (a-a_f)^2 + \frac{1}{2} k_f c^2 + \omega_f (a-a_f)\, c$$

comparing $f(a,c)$ from (i) and (ii) and equating coefficients we get:

$\lambda_f = \lambda_e \equiv \lambda$; $k_f = k_e \equiv k$; $\omega_f = \omega_e \equiv \omega$

$a_f = a_e + \frac{\omega c_e}{\lambda}$, $c_f = c_e \left(1 - \frac{\omega^2}{k\lambda}\right)$

$a_f > a_e$ if $\omega c_e > 0$; c_f and c_e same sign ($k\lambda > \omega^2$)

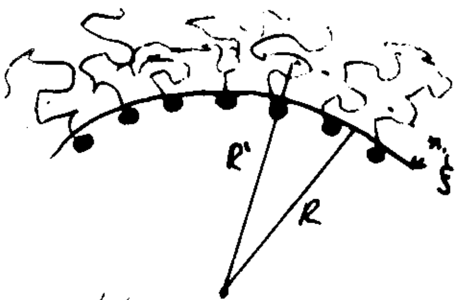
There are other choices for reference state

(iii) tensionless at optimal curvature

(iv) flat with $\frac{\partial f}{\partial c} \neq 0$ $\frac{\partial f}{\partial a} \neq 0$

up to quadratic order there are relations among the parameters.

The surface of inextension or neutral surface:



free energy for a flat surface with area per molecule a_0; $\frac{\partial f}{\partial c} = -k_0 c_0$

$$\frac{\partial f}{\partial a} = \gamma_0$$

$$f(a,c) = f(a_0,0) + \gamma_0 (a - a_0) + \frac{1}{2} \lambda_0 (a - a_0)^2$$
$$- k_0 c_0 c + \frac{1}{2} k_0 c^2 + \omega_0 (a - a_0) c$$

in f a and c are measured from the interface.

for a cylindrical deformation (around $c \sim 0$)

$$c' = \frac{1}{R'} = \frac{1}{R+\xi} = \frac{1}{R}\left(\frac{1}{1+\frac{\xi}{R}}\right) = c(1 - c\xi)$$

$$a' = a\left(1 + \frac{\xi}{R}\right) \Rightarrow c = c' + c'^2 \xi \,;\; a = a'(1 - c'\xi)$$

replacing c and a in f we get:

$$f(a,c) = f(a_0,0) + \gamma_0 (a' - a_0) + \frac{1}{2} \lambda_0 (a' - a_0)^2 - (k_0 c_0 + \gamma_0 a_0 \xi) c'$$
$$+ \left(\frac{1}{2} k_0 - k_0 c_0 \xi + \frac{1}{2} \lambda_0 a_0^2 \xi^2 - \omega_0 a_0 \xi\right) c'^2 + (\omega_0 - \gamma_0 \xi - \lambda_0 a_0 \xi)(a' -$$

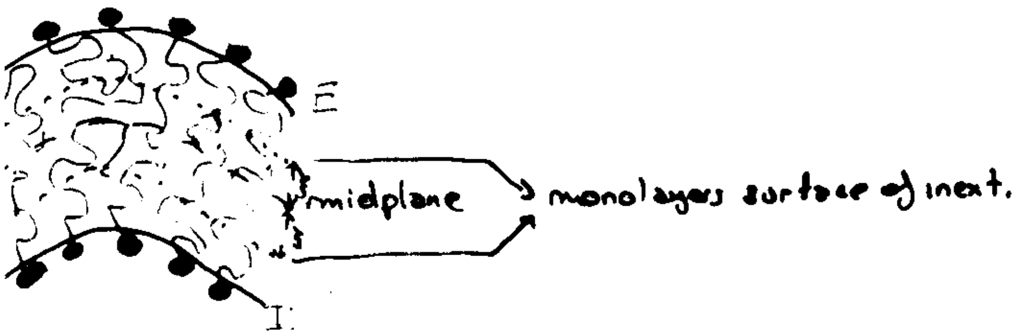
if we choose $\xi = \frac{\omega_0}{\gamma_0 + \lambda_0 a_0}$ the cross term vanishes ξ determines the distance of the neutral surface from the interface.

"renormalized constants":

$$f(a,c) = f(a_0,0) + \gamma_0 (a' - a_0) + \frac{1}{2} \lambda (a' - a_0)^2$$
$$- \left(k_0 c_0 + \frac{\gamma_0 a_0 \omega_0}{\gamma_0 + \lambda_0 a_0}\right) c'$$
$$+ \underbrace{\left(\frac{1}{2} k_0 + \frac{1}{2} \lambda_0 a_0^2 \frac{\omega_0^2}{(\gamma_0 + \lambda_0 a_0)^2} - \frac{\omega_0 (k_0 c_0 + \omega_0 a_0)}{\gamma_0 + \lambda_0 a_0}\right)}_{\text{effective bending constant!!}} c'^2$$

What about bilayers?

Let's consider the bilayer's free energy in terms of the monolayers' free energy:



Monolayer's free energy (c, a from neutral surface)

$$f_{\substack{E\\I}}(c_1, c_2, a) = f(0,0,a_0) + \gamma(a_{\substack{E\\I}} - a_0) + \frac{\lambda}{2}(a_{\substack{E\\I}} - a_0)^2$$
$$- 4k h_0 h_{\substack{E\\I}} + 2k h_{\substack{E\\I}}^2 + \bar{k} g_{\substack{E\\I}}$$

$h = \frac{c_1 + c_2}{2}$ "mean curvature" $\quad g = c_1 c_2$ "Gaussian curvature"

$$h = h' - \frac{\xi}{2} h'^2 + \xi g' \qquad \text{' measured at midplane}$$
$$a = a'[1 + 2\xi h' + \xi^2 g']$$

$$f(h', g', a') = f(0,0,a_0) + \gamma(a' - a_0) + \frac{\lambda}{2}(a' - a_0)^2 + 2w(a' - a_0)h'$$
$$- 4k h_0' h' + 2k' h'^2 + \bar{k}' g'$$

$\bar{k}' = \bar{k} - 4h_0 k\xi + \gamma a_0 \xi^2$

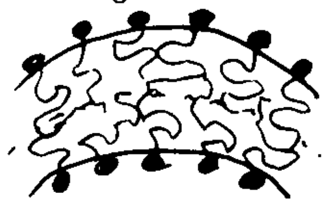
$= \gamma\xi + \lambda a_0 \xi;\ h_0' = h_0 - \gamma a_0 \xi / 2k;\ k' = k(1 + \xi h_0) + \lambda a_0^2 \xi^2;$

Bilayer's free energy: (symmetric)

$$f_{total} = \underbrace{\frac{a_E}{a_E + a_I}}_{x_E} f_E + \underbrace{\frac{a_I}{a_E + a_I}}_{x_I = 1 - x_E} f_I$$

Minimize free energy wrt area subject to constraint $\mu_E = \mu_I$ at all curvatures

$$f_{min} = f_0 - \frac{\gamma^2}{2\lambda} + \frac{1}{2} K_{eff} h^2 + \bar{K}_{eff}\, g$$



(exactly as Helfrich's expression!!)

$$K_{eff} = 2(k + k h_0 \xi + \lambda a_0^2 \xi^2) - \underbrace{\frac{2\lambda\left[(\gamma + \lambda a_0) a_0 \xi + 2\left(h_0 - \frac{\gamma a_0 \xi}{2k}\right)(k + k h_0 \xi + \lambda a_0^2 \xi^2)\right]^2}{(\lambda a_0 - \gamma)^2}}_{\text{reduces the effective bending from } 2k_m \text{ (flip-flop!!)}}$$

$$\bar{K}_{eff} = \bar{k} - 4k h_0 \xi + \gamma a_0 \xi^2$$

Optimal area per molecule of the "monolayers"

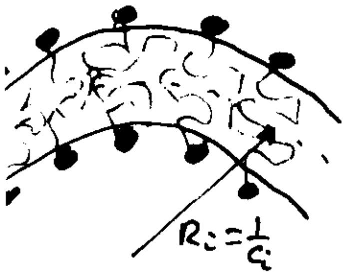
$$a_{\substack{E\\I}} = a_0 - \frac{\gamma}{\lambda} \mp \frac{2h\left[(\gamma + \lambda a_0) a_0 \xi + 2\left(h_0 - \frac{\gamma a_0 \xi}{2k}\right)(k + k h_0 \xi + \lambda a_0^2 \xi^2)\right]}{\lambda a_0 - \gamma}$$

Looking at bilayers:

Reference state: planar film ($H = G = 0$);

tensionless $\left(\frac{\partial f}{\partial a} = 0\right)$ and symmetric $\left(x_E = x_I = \frac{1}{2}\right)$

New variable $x = x_E - \frac{1}{2} = \frac{1}{2} - x_I$ (flip-flop)



$$\frac{\delta f}{A_0} = \frac{1}{2}\Lambda(a-a_0)^2 + 2KH^2 + \bar{K}G$$

$$+ \frac{1}{2}\sigma x^2 + 2\mu x H$$

$$H = \frac{c_1 + c_2}{2} = \frac{c_+}{2} \qquad G = c_1 c_2 = \frac{c_+^2 - c_-^2}{4} \qquad c_- = c_1 - c_2$$

symmetric bilayer: midplane = surface of inextension

and no terms linear in c_- $[f(c_-) = f(-c_-)]$; c_+

due to symmetry $[f(c_+) = f(-c_+)]$

Modes of deformation:

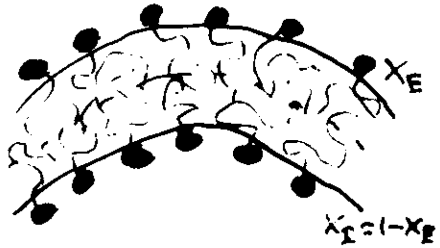
$x = 0 \Rightarrow$ blocked exchange

$\frac{\partial \delta f}{\partial x} = 0 \Rightarrow$ free exchange ($\mu_E = \mu_I$ for all c)

To keep the expansion to second order in c:

$$x = \frac{\partial x}{\partial c_+} c_+ = \frac{\partial x_E}{\partial c_+} c_+ = \eta\, c_+$$

η = "relaxation variable"



$$\frac{\delta f}{A_0} = \frac{1}{2}\Lambda(a-a_0)^2 + \frac{1}{2}K(\eta)c_+^2 + \frac{1}{4}\bar{K}(c$$

$K(\eta) = K_b + K_c\,\eta + K_s\,\eta^2$

"stretching"

"block exchange"

"composition-curvature coupling"

$$\Lambda = \frac{1}{a_0}\left(\frac{\partial^2 f}{\partial a^2}\right)_{c_+ = c_- = 0;\ \eta = 0}$$

$$\bar{K} = -\frac{2}{a_0}\left(\frac{\partial^2 f}{\partial c_-^2}\right)_{c_+ = c_- = 0;\ \eta = 0;\ a = a_0}$$

$$K_b = \frac{1}{a_0}\left[\left(\frac{\partial^2 f}{\partial c_+^2}\right)_{c_+ = c_- = 0;\ \eta = 0;\ a = a_0} + \left(\frac{\partial^2 f}{\partial c_-^2}\right)_{c_+ = c_- = 0;\ \eta = 0;\ a = a_0}\right]$$

$$K_c = \frac{2}{a_0}\left(\frac{\partial^2 f}{\partial x_E \partial c_+}\right)_{c_+ = c_- = 0;\ a = a_0} \quad ; \quad K_s = \frac{1}{a_0}\left(\frac{\partial^2 f}{\partial x_E^2}\right)_{c_+ = c_- = 0;\ a = a_0}$$

Methods of calculation:

) Direct evaluation.

(i) cylindrical deformation, i.e. $c_1 = c,\ c_2 = 0$

$$\frac{f}{a} = \frac{1}{2} k (c - c_0)^2$$

(ii) saddle deformation, i.e. $c_1 = -c_2 = c$

$$\frac{f}{a} = -\bar{k} c^2 + \frac{1}{2} k c_0^2$$

(Relaxation of the molecules?)

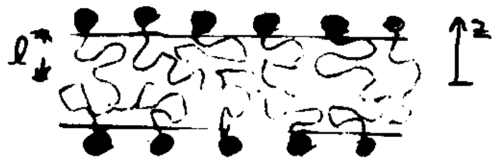
Microscopic evaluation of the elastic constants

Bilayer's free energy: (packing)

$$\beta f = -x_E \ln q_E - (1 - x_E) \ln q_I - \int \pi(z)\, a(z)\, dz$$

$$q_{\frac{E}{I}} = \sum_{\alpha_{\frac{E}{I}}} e^{-\beta \varepsilon_{int}(\alpha_{\frac{E}{I}}) - \int \pi(z')\, \eta_{\frac{E}{I}}(z'; \alpha_{\frac{E}{I}})\, dz'}$$

$$\Lambda = \frac{1}{a_0} \int \left(\frac{\partial \pi(z)}{\partial a}\right)_{c_+ = c_- = 0;\ \eta = 0} dz$$



$$\bar{K} = -\int \pi(z)\, z^2\, dz$$

$$\frac{f}{a_0} = \frac{1}{2} \Lambda (a - a_0)^2 + \frac{1}{2} K(\eta) c_+^2 + \bar{K} (c_+^2 - c_-^2)$$

$$K(\eta) = K_b + \eta K_c + \eta^2 K_s$$

$$K_b = -\int \left(\frac{\partial \pi(z)}{\partial c_+}\right)_{c_+ = c_- = 0;\ \eta = 0} z\, dz$$

$$K_c = -\ell \int \left(\frac{\partial \pi(z)}{\partial x_E}\right)_{c_+ = c_- = 0} z\, dz$$

$$K_s = \frac{\ell^2}{4 a_0} \int \left(\frac{\partial \pi(z)}{\partial x_E}\right)_{c_+ = c_- = 0} \left[\langle n_E(z) \rangle - \langle n_I(z) \rangle\right] dz$$

Everything evaluated at the planar film!!

How do we find the derivatives of π

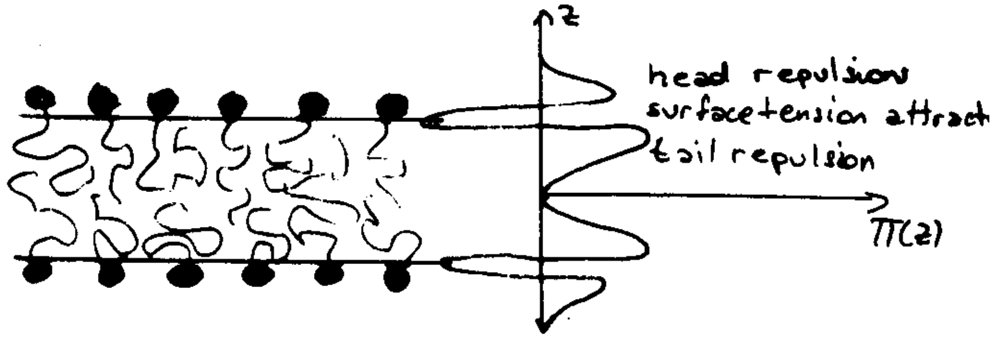
differentiate the packing constraint:

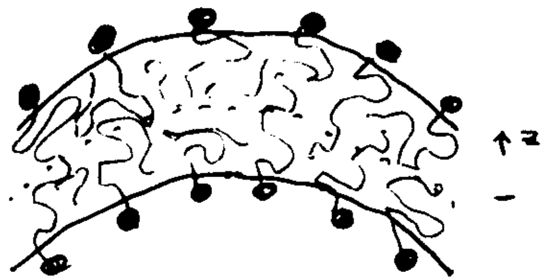
$$\frac{\partial}{\partial c_+}\left[\sum_{\alpha}\frac{e^{-\beta\epsilon_{int}(\alpha)-\int\pi(z')n(z';\alpha)dz'}}{q}\, n(z,\alpha)\, a_s = a(z)\right]$$

$$a(z) = a(0)\left[1+z c_+ + \frac{z^2}{4}(c_+^2-c_-^2)\right]$$

$$\int\left(\frac{\partial\pi(z')}{\partial c_+}\right)_{c_+=c_-=0}\left[\langle n(z')\rangle\langle n(z)\rangle-\langle n(z')n(z)\rangle\right]dz' = a(0)z$$

$\langle n(z')\rangle\langle n(z)\rangle - \langle n(z')n(z)\rangle$ intramolecular "density-density" correlation function.





$$\frac{\partial\pi(z)}{\partial c_+} < 0 \text{ for } z>0$$

$$\left(\frac{\partial\pi(z)}{\partial c_+} > 0 \text{ for } z<0\right)$$

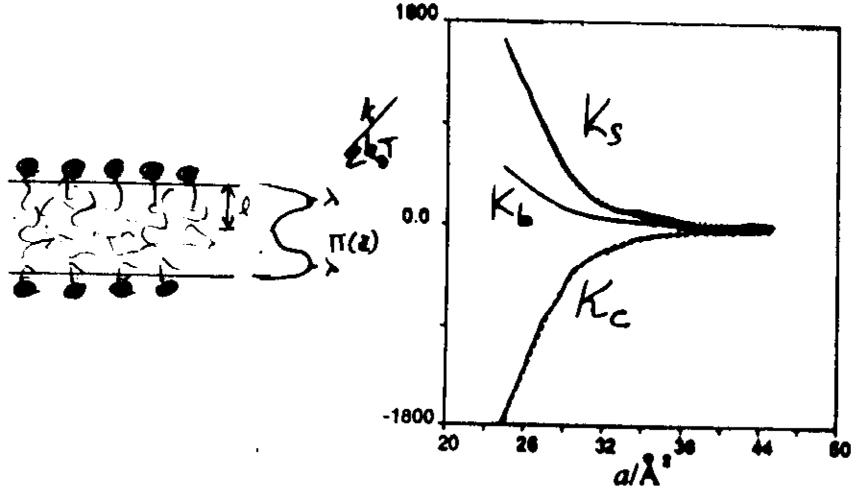
$$K_b = -\int\frac{\partial\pi(z)}{\partial c_+}\, z\, dz > 0$$ tails and head repulsions

$$\left(\frac{\partial\pi(z)}{\partial x_e}\right)_{c_+=c_-=0} > 0 \text{ for } z>0\ ;\ <0 \text{ for } z<0$$

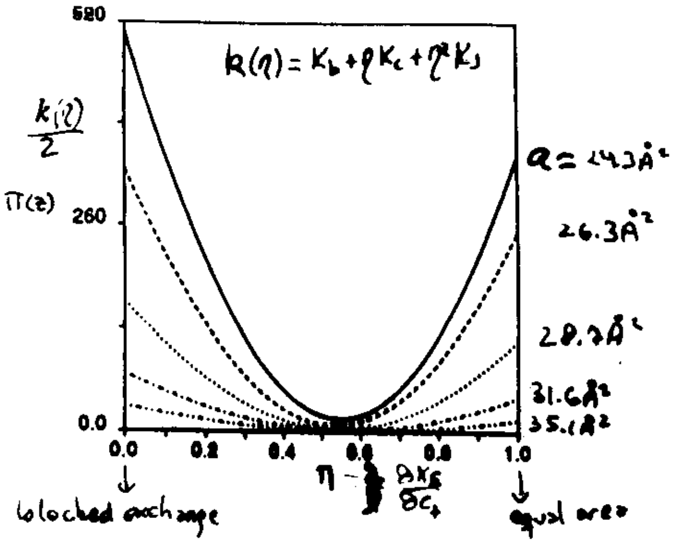
$$K_c = -\ell\int\left(\frac{\partial\pi(z)}{\partial x_e}\right)_{c_+=c_-=0} z\, dz < 0$$ (relaxation)

$\pi(z)$ tails + heads $\Longrightarrow \bar{K} = +\int\pi(z)z^2dz < 0$
surface tension $\bar{K} > 0$

Tail's contribution: Bilayer $H-(CH_2)_{15}-CH_3$

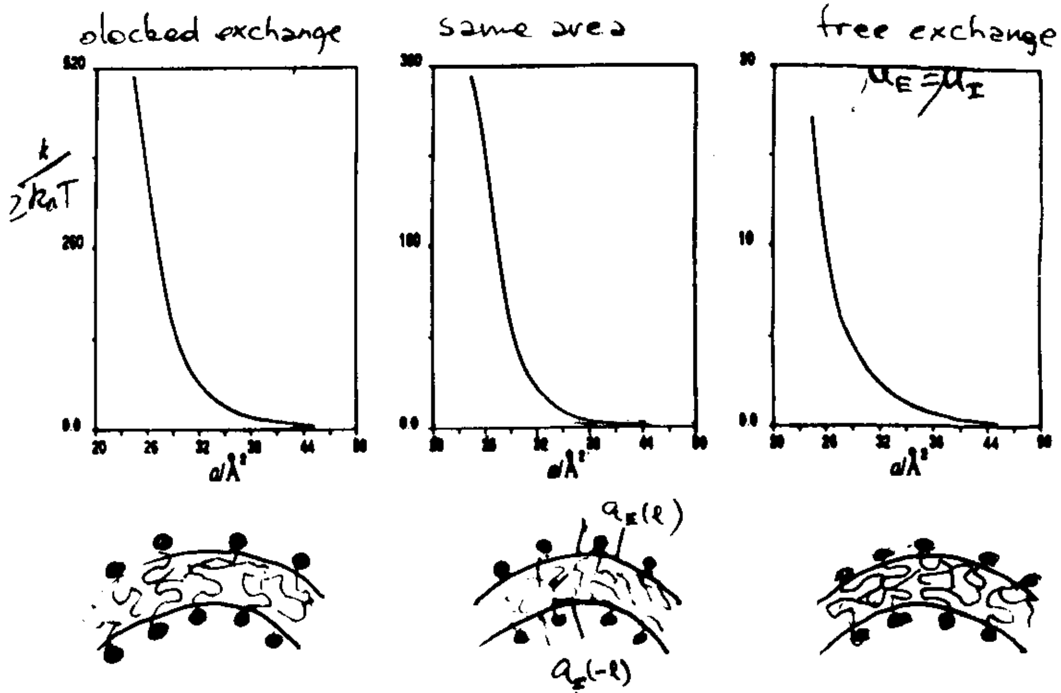


min $\Rightarrow$ λ = maximum $\Pi(z)$



Bilayer bending constant for different mode of deformation (tails contribution).

$H-(CH_2)_{15}-CH_3$



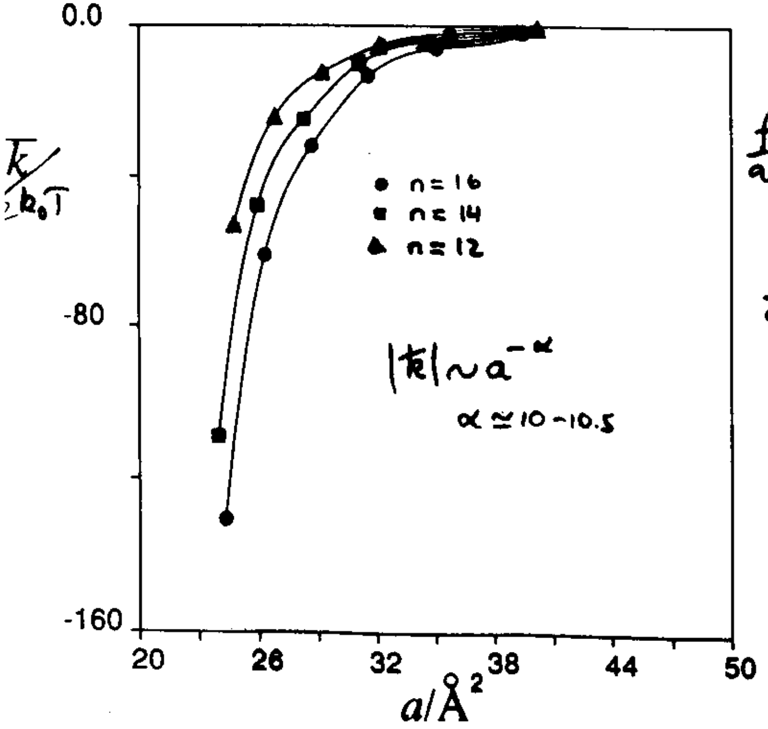
$N_E = N_I$ for all c

$a_E(l) = a_I(-l)$ for all c

minimal f for all c

$$k \propto n^3 a^{-7.5}$$

Bilayer, $\bar{k} = -\int \pi(z) z^2 dz$



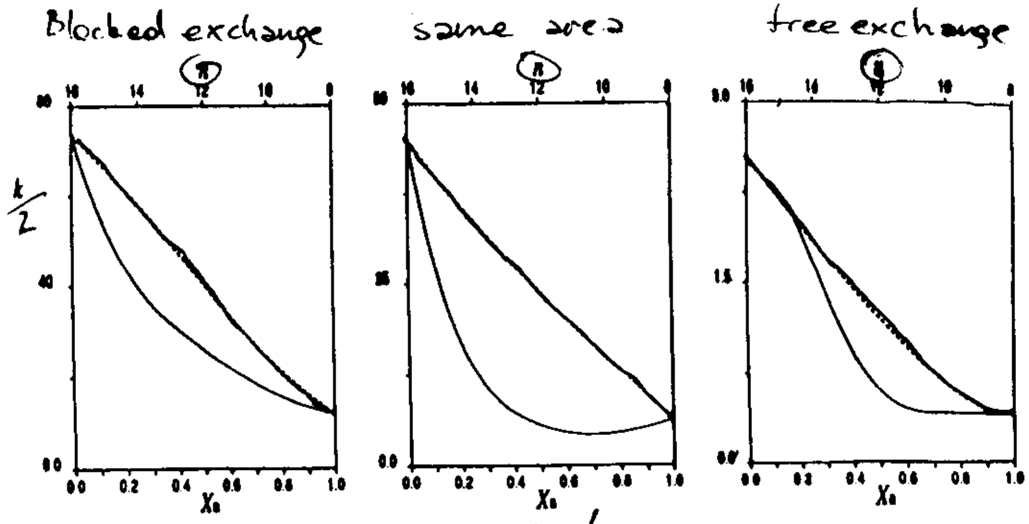
$$\frac{f}{a} = \frac{1}{2}k(c_1+c_2) + \bar{k}c_1c_2$$

$$c_1 = -c_2 \equiv c$$

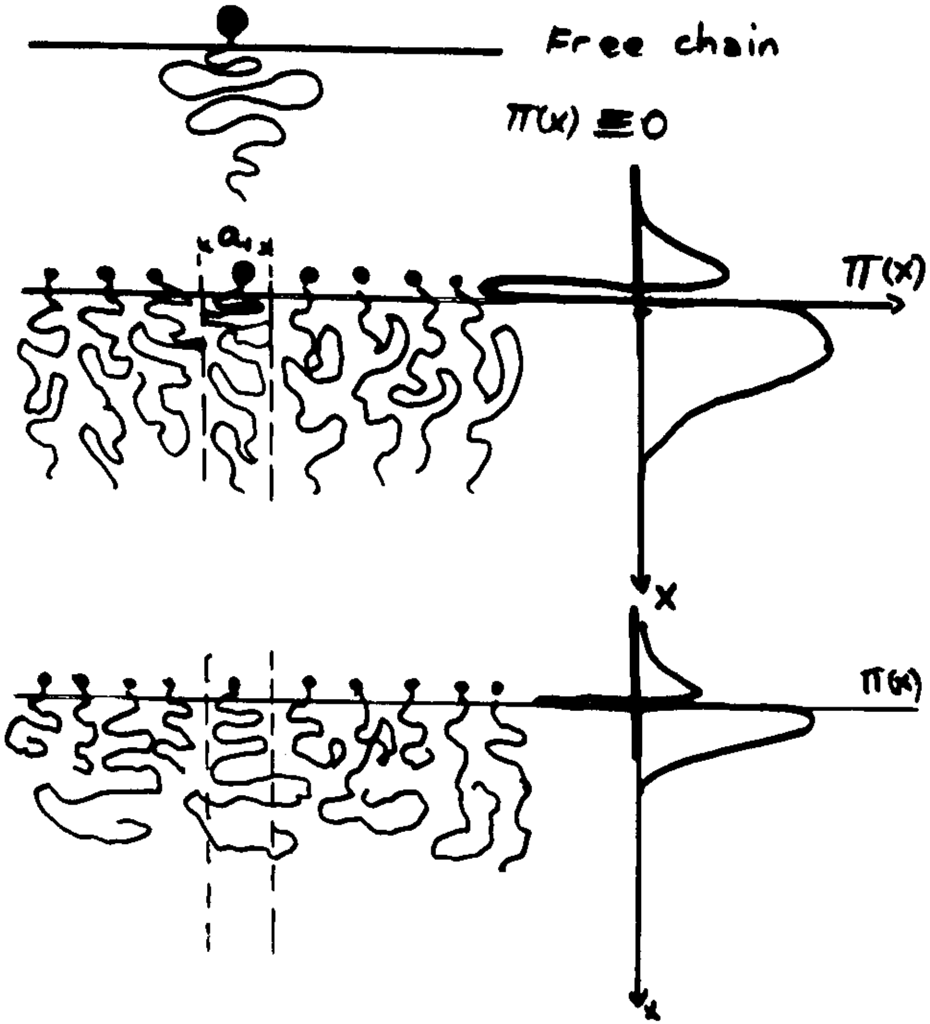
$$\frac{f}{a} = -\bar{k}c^2$$

Bending constants in mixed bilayers

$a = 31.6\,\text{Å}^2$



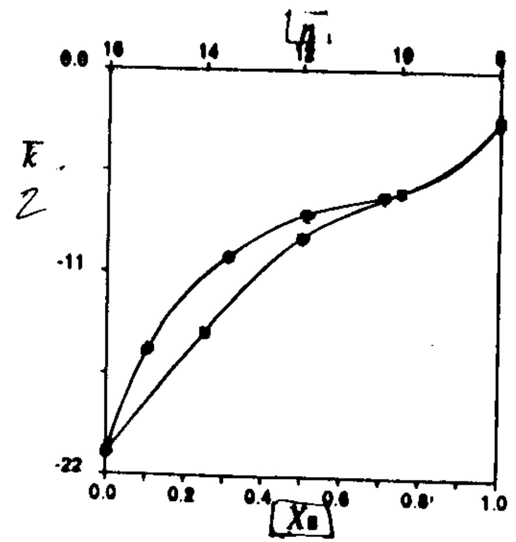
C_{16}/C_8



1) Magnitude of $\pi(x)$

2) Place of maximal pressure

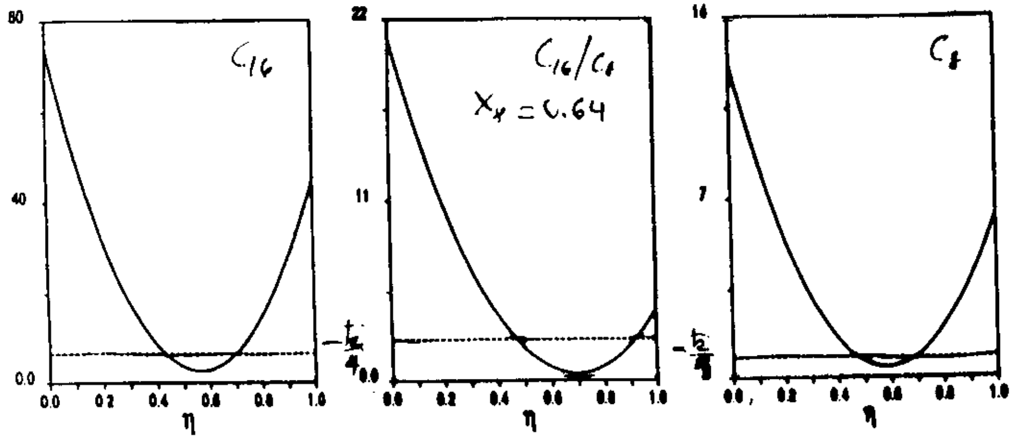
Saddle-Splay constant $a = 31.6 Å^2$



Planar bilayer stability (tails)

$$\frac{f}{a} = \frac{1}{2} k c_+^2 + \frac{\bar{k}}{4}\left(c_+^2 - c_-^2\right) \qquad a = 31.6\,\text{Å}^2$$

$$k > -\frac{\bar{k}}{2} > 0$$



What do the head-groups and surface tension contribute?

(iii) Electrostatic Contribution:

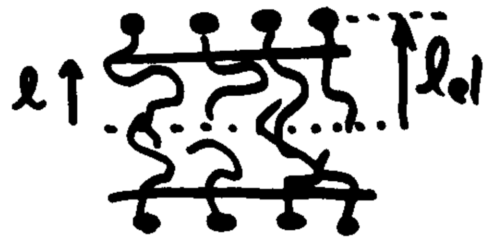
Solve Poisson-Boltzmann equation:

(Lekkerkerker; Mitchell and Ninham)

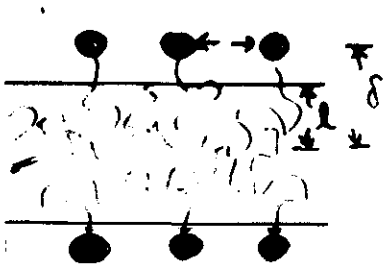
$$f^{el}_{E,I} = \left(\frac{kT}{e}\right)^2 \varepsilon_r \varepsilon_0 \kappa \left[\left\{ 4\left(p_{E,I} \ln\left(p_{E,I} + q_{E,I}\right) - q_{E,I} + 1\right)\right\} \mp \frac{4}{\kappa} \ln\left[\frac{q_{E,I}+1}{2}\right] c + \frac{4}{\kappa^2} \left\{ \frac{\left(q_{E,I}-1\right)\left(q_{E,I}+2\right)}{q_{E,I}\left(q_{E,I}+1\right)} - \int_{z=\frac{1}{1+q_{E,I}}}^{1} \frac{\ln z}{z-1}\, dz \right\} c^2 \right]$$

$$p_{E,I} = \frac{2\pi Q}{\kappa\, a_{E,I}(c)} \; ; \quad q_{E,I} = \sqrt{p_{E,I}^2 + 1}$$

$$a_{E,I}(c) = \frac{a(0)}{2 x_{E,I}} \left[1 \pm 2 \ell_{el} c + \ell_{el}^2 c^2 \right]$$



Opposing forces (Tanford, Israelachvili, Ninham, Mitchell)



$\gamma a(l)$ surface tension

$\frac{c}{a(\delta)}$ repulsion

planar film $\rightarrow$ $f = \gamma a + \frac{c}{a} \Rightarrow a_h = \sqrt{\frac{c}{\gamma}}$

$$f_{bil} = x_E f_E + (1-x_E) f_I$$

$$f_E = \gamma a_E(l) + \gamma \frac{a_h^2}{a_E(\delta)} \quad ; \quad f_I = \gamma a_I(-l) + \gamma \frac{a_h^2}{a_I(-\delta)}$$

$$a_E(l) = \frac{a(0)}{2x_E}\left(1 + l c_+ + \frac{l^2}{4}(c_+^2 - c_-^2)\right); \quad a_I(-l) = \frac{a(0)}{2(1-x_E)}\left(1 - l c_+ + \frac{l^2}{4}(c_+^2 - c_-^2\right.$$

$$= \gamma \delta^2 \left(\frac{a_h}{a(0)}\right)^2 \quad > 0$$

$$= -2\gamma \left(\frac{a_h}{a(0)}\right)^2 \delta l \quad < 0$$

$$= \gamma l^2 \left(\frac{a_h}{a(0)}\right)^2 \quad > 0$$

$$= \frac{\gamma}{2} l^2 \left(1 - \left(\frac{a_h}{a(0)}\frac{\delta}{l}\right)^2\right) \quad > 0$$

$H-(CH_2)_{15}-CH_3$

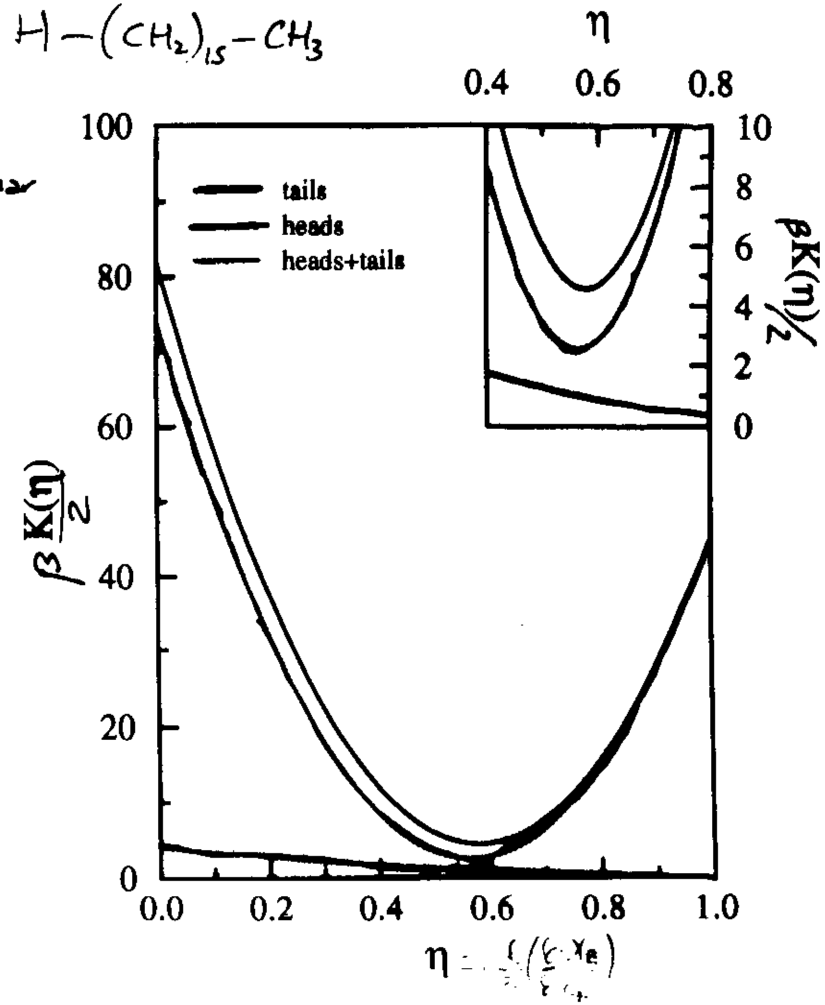
minimal free energy for planar film w.r.t. a

$= 0.15 \frac{kT}{Å^2}$

$= 16 Å^2$

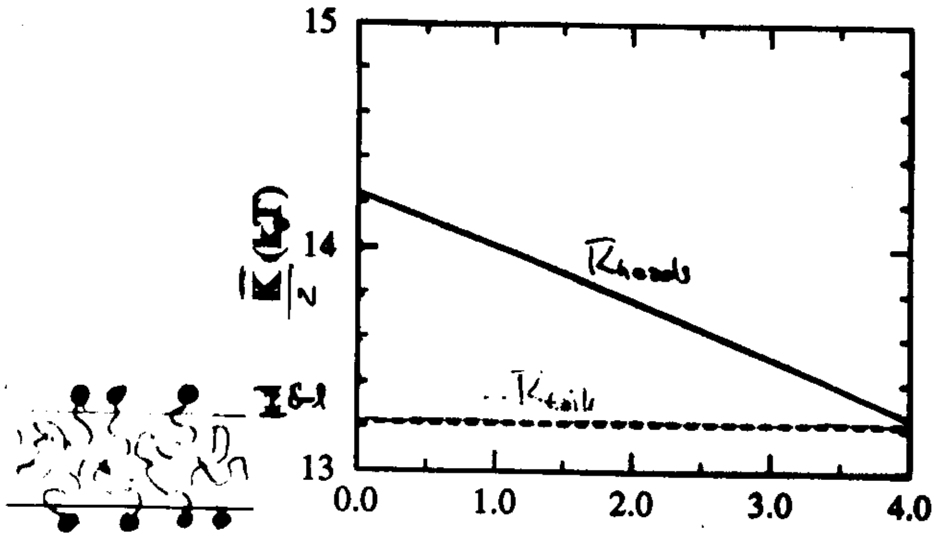
$a(0) = 31.6 Å^2$

$= l + 2Å$



only for free exchange head contributions are important in determining $K(\eta)$

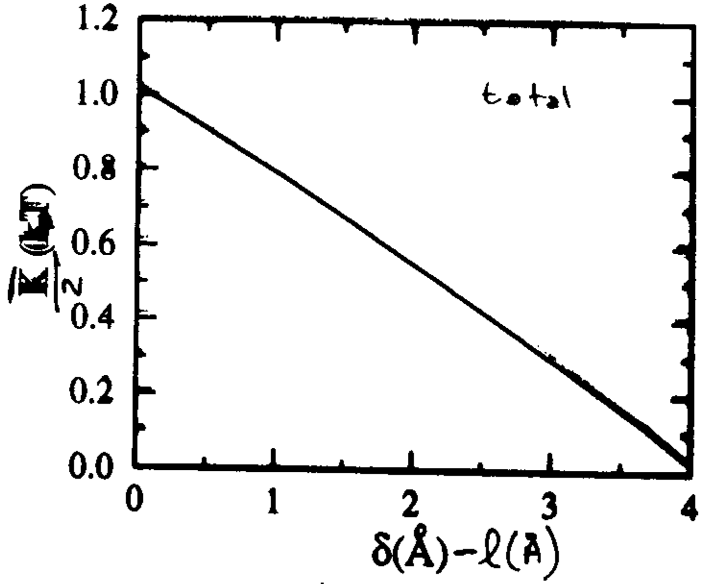
$H-(CH_2)_{15}-CH_3$



: c . (K b_0 ?) Å

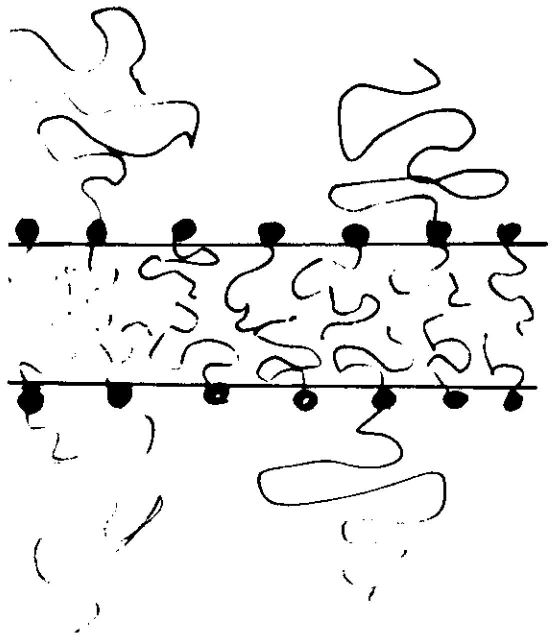
: 1L Å²

) = 31.6 Å²



$\bar{\kappa} > 0$ spontaneous(?) saddle deformation (cubic phase)

Polymer decorated bilayers:



Two independent composition variables

$\eta_{tail/head}$ η_{poly}

$$K(\eta_{tail/head}, \eta_{poly}) = K_{b,tail/head} + \eta_{tail/head} K_{c,tail/head} + \eta_{t/h}^2 K_{s,t/h} + K_{b,poly} + \eta_{poly} K_{c,poly} + \eta_{poly}^2 K_{s,poly}$$

$$\bar{K}_{total} = \bar{K}_{t/h} + \bar{K}_{poly}$$

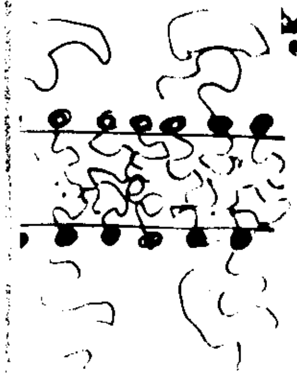
Possible spontaneous vesicle formation:

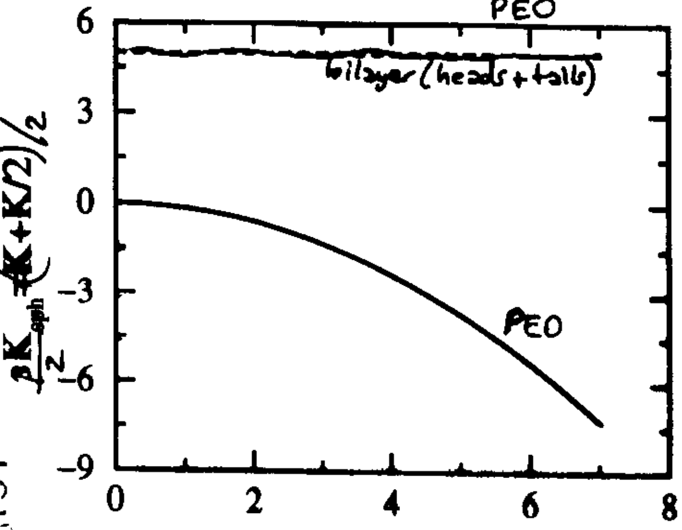
$$K_{sph} = K(\eta_{tail/head}, \eta_{poly}) + \frac{\bar{K}_{total}}{2} < 0$$

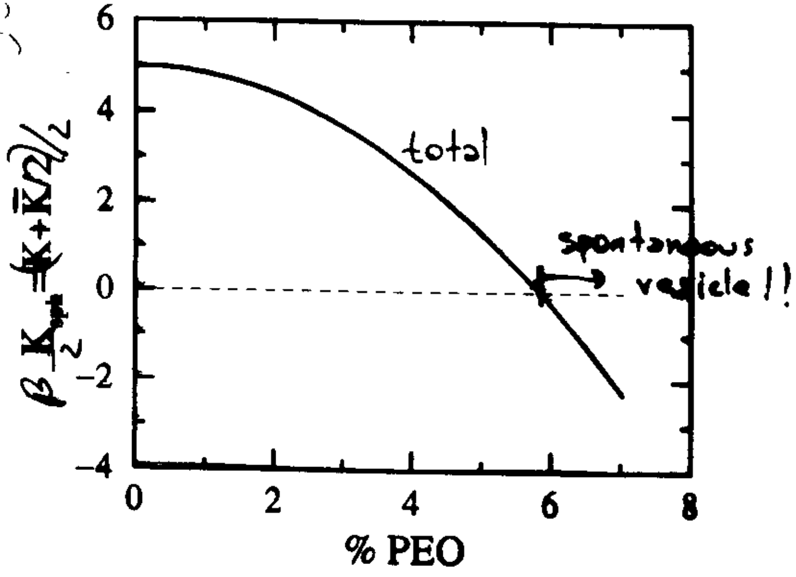
Mixed $H-(CH_2)_{15}-CH_3$ / $\underbrace{(CH_2-CH_2-O)_{50}}_{PEO}-H-(CH_2)_{15}-CH_3$

$= \frac{1}{2} K_{sph} c^2$

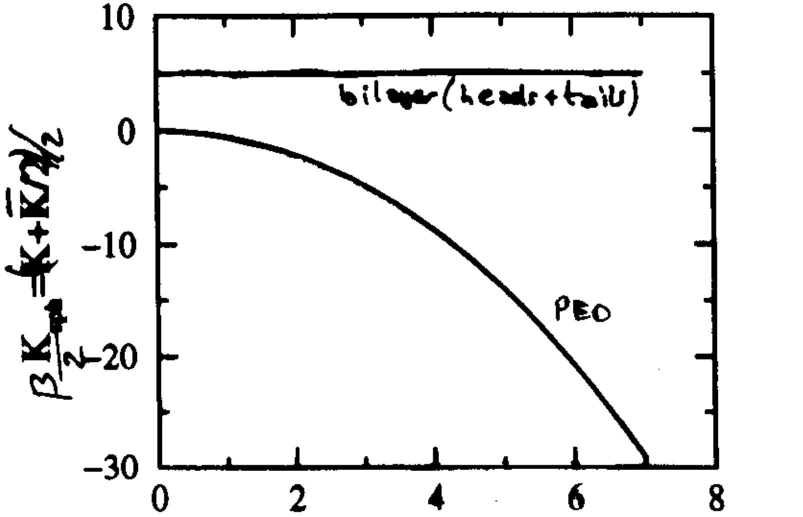
if $K_{sph} < 0$
unstable planar

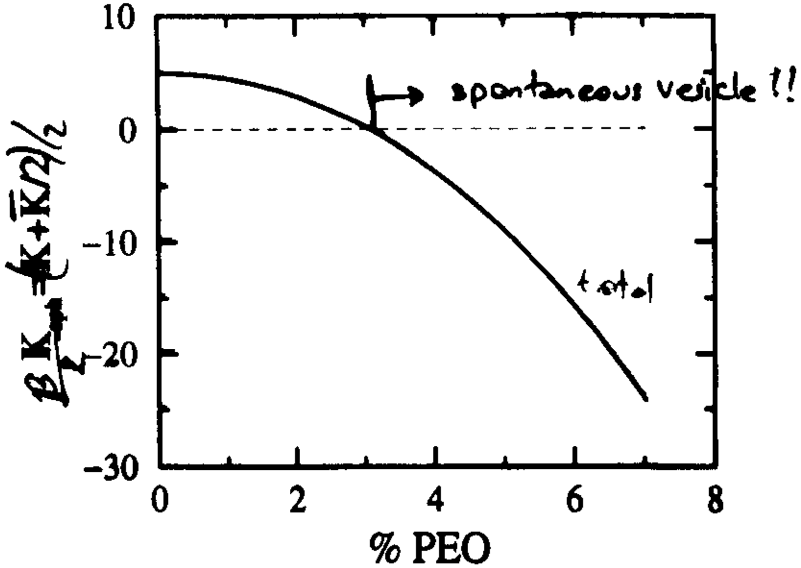






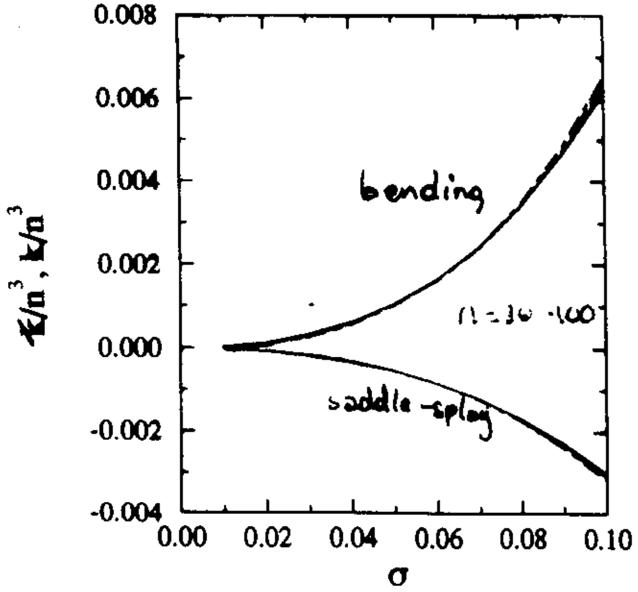
Mixed $H-(CH_2)_{15}-CH_3$ / $(CH_2-CH_2-O)_{100}-H-(CH_2)_{15}-CH_3$

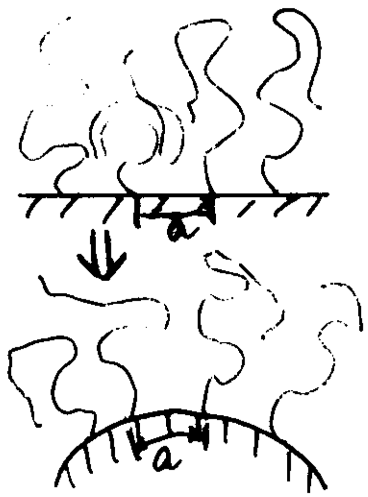


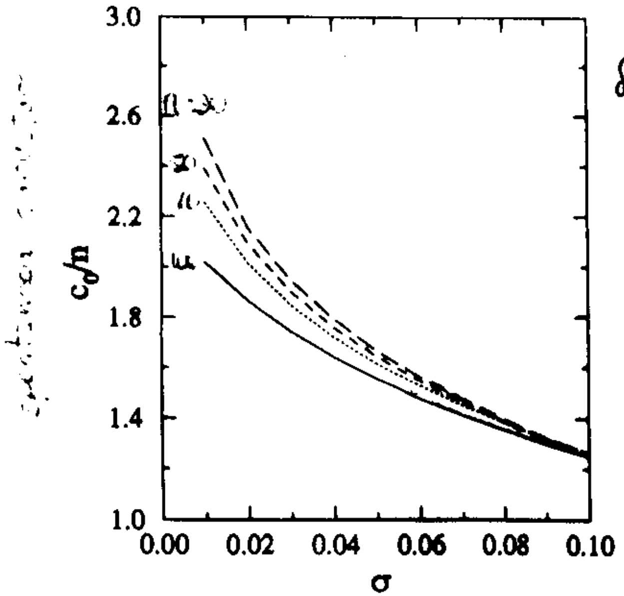


Larger n lower % needed

Elastic Constants (for fixed area at surface)







$$\frac{\delta f}{a} = \underbrace{-k c_0 c_+}_{} + \frac{1}{2}\left(k + \frac{\bar{k}}{2}\right) c_+^2 - \frac{\bar{k}}{4} c_-^2$$

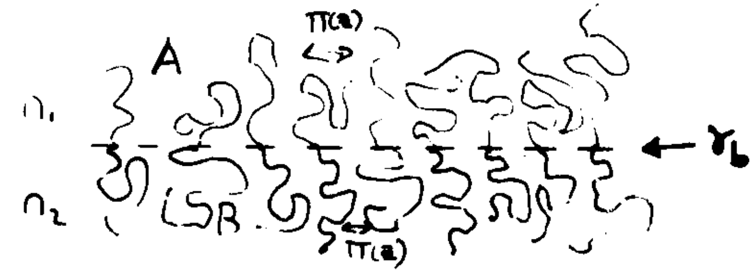
dominant term for fixed area.

Diblock Copolymers at Liquid-Liquid interface

γ_b is the bare liquid-liquid surface tension.

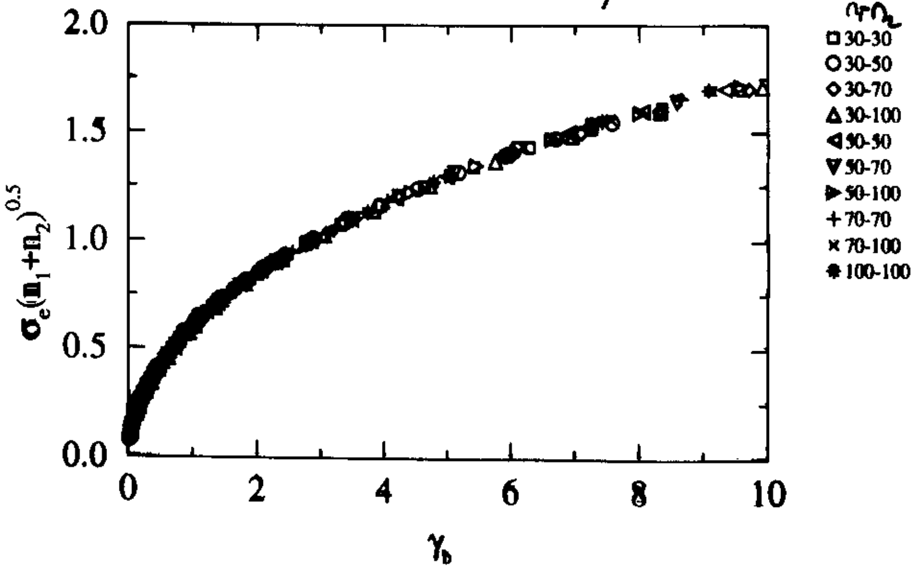
We assume that <u>all</u> the diblock is at the interface and minimize the surface free energy.

$\Rightarrow$ equilibrium surface coverage as a function of γ_b (corresponds to zero surface tension)

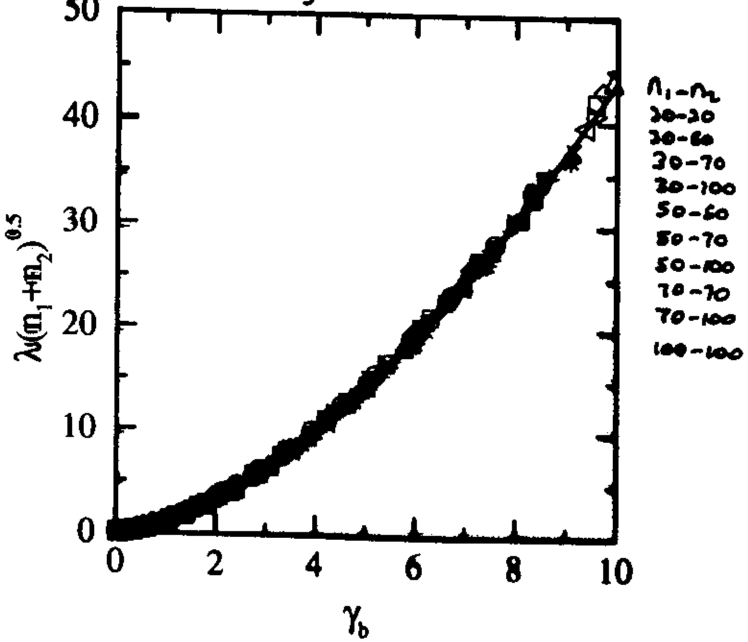


Universal surface coverage

$\sigma_e = \frac{1}{a_e}$



Stretching constant



$$\lambda = -\int \left(\frac{\partial \Pi(z)}{\partial n}\right)_{a_e} dz$$

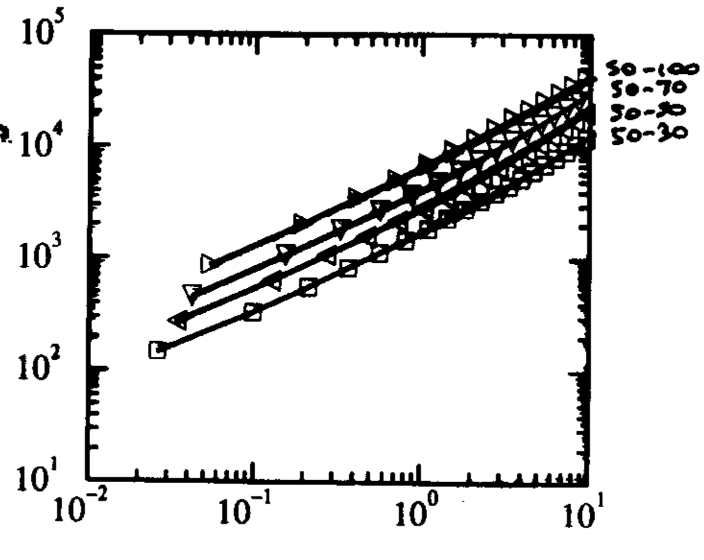
$$\lambda\,(n_1+n_2)^{1/2} \propto \gamma_b^{1.6}$$

$$\Pi'(z) = \Pi(z) + e^{-\Pi(z)} - 1$$

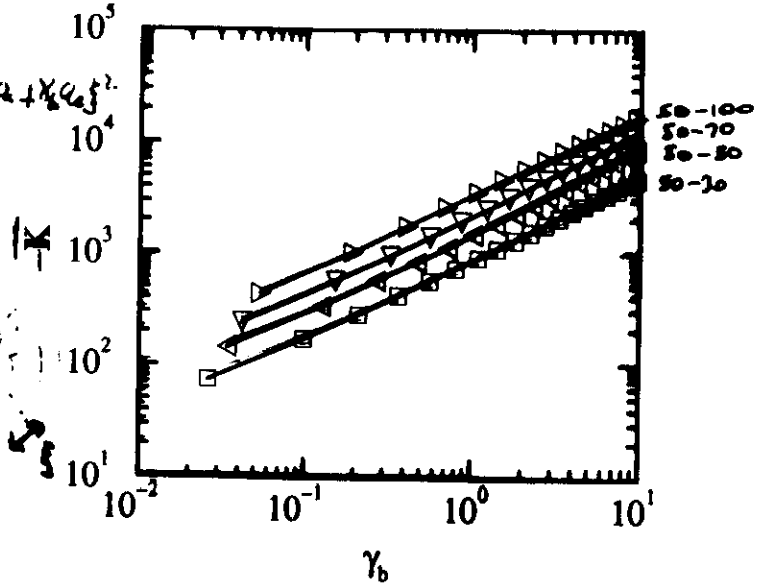
Bending and saddle-splay constants diblock copolymers

$$= -a_e \int \left(\frac{\partial \Pi(z)}{\partial a_e}\right)_{a_e, q_0} z\, dz$$

$$(z) = \Pi(z) + e^{-\Pi(0)} - 1$$

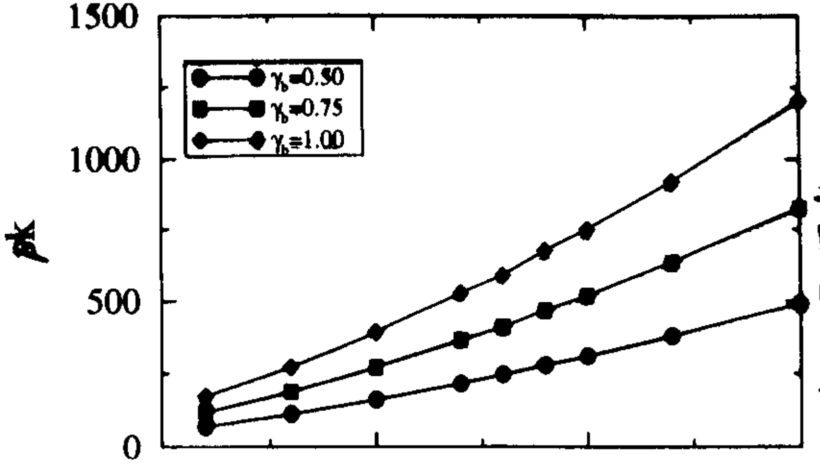


$$= a_e \int \Pi(z)\, z^2 dz + \chi_a a_e \xi^2$$

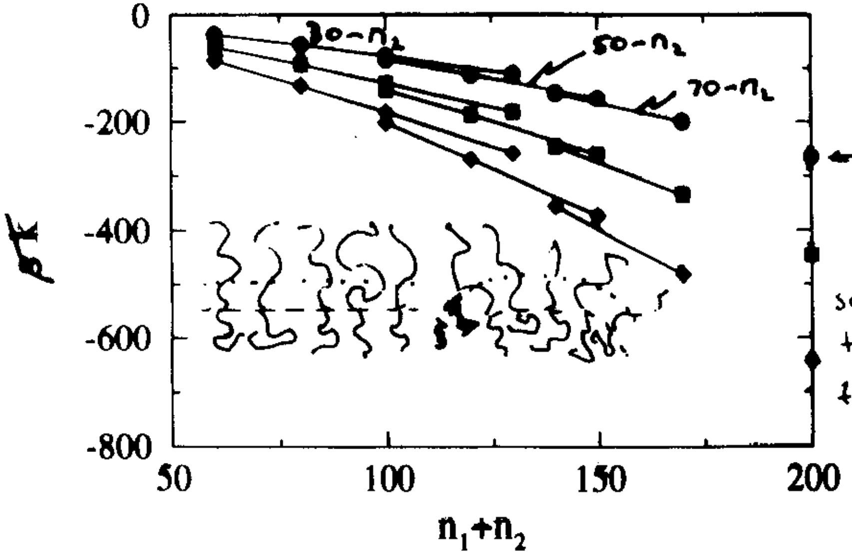


Elastic Constants

$e^{-\Pi(z)}-1+\Pi(z)$ $\quad k = -\int_{-\infty}^{\infty} \frac{\partial \Pi(z)}{\partial c_+}\, z\, dz \quad \bar{k} = -\int_{-\infty}^{\infty} \Pi(z)\, z^2\, dz + \gamma_b \zeta^2$



$k \propto n^{1.6}$ as predicted by Cantor ($n = n_1 + n_2$) but no γ_b scaling found.

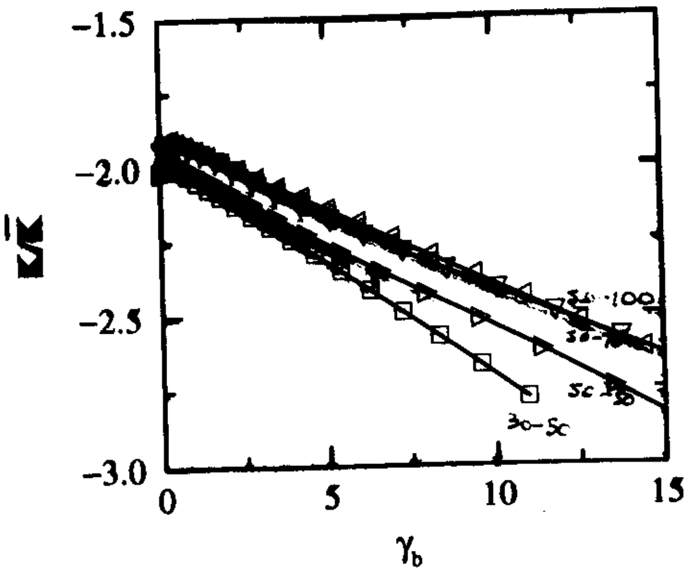


← 100-100

$\bar{k}$ does not scale due to the two contributions.

ζ = distance between surface of inextension and interface.

Diblock copolymers

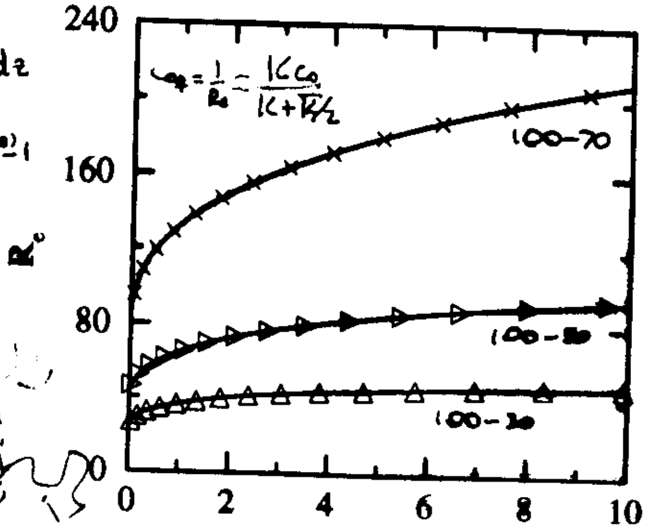


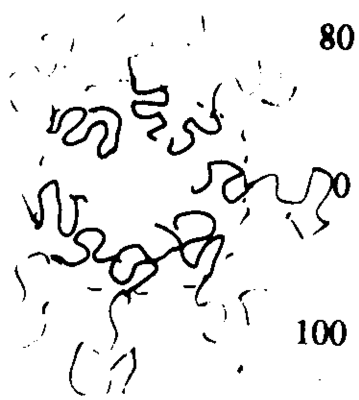
Ratio is strongly dependent on $\gamma_b \Leftrightarrow$ effect on phase behavi

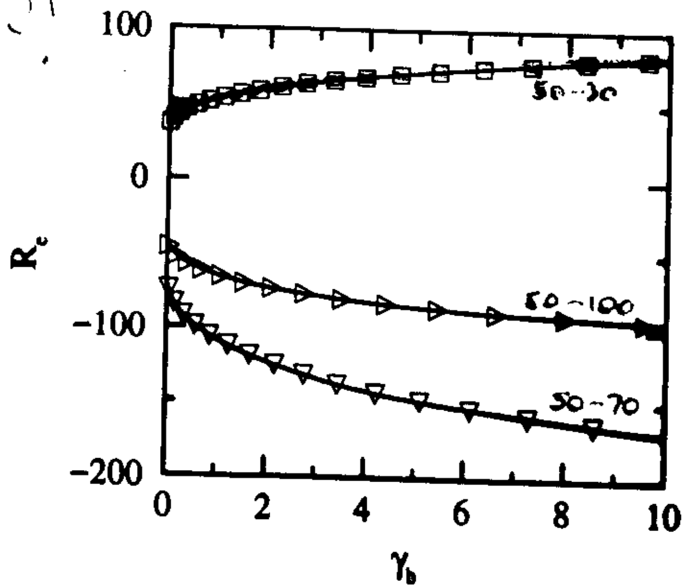
Spontaneous radii in diblock copolymers

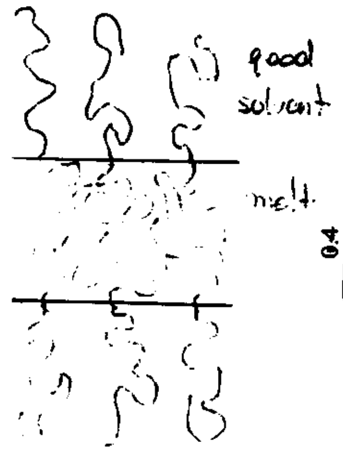
$\kappa c_0 = a_e \int_{-\infty}^{\infty} \tilde{\Pi}(z)\, z\, dz$

$\tilde{\Pi}(z) = \pi(z) + e^{-\pi(z)} - 1$



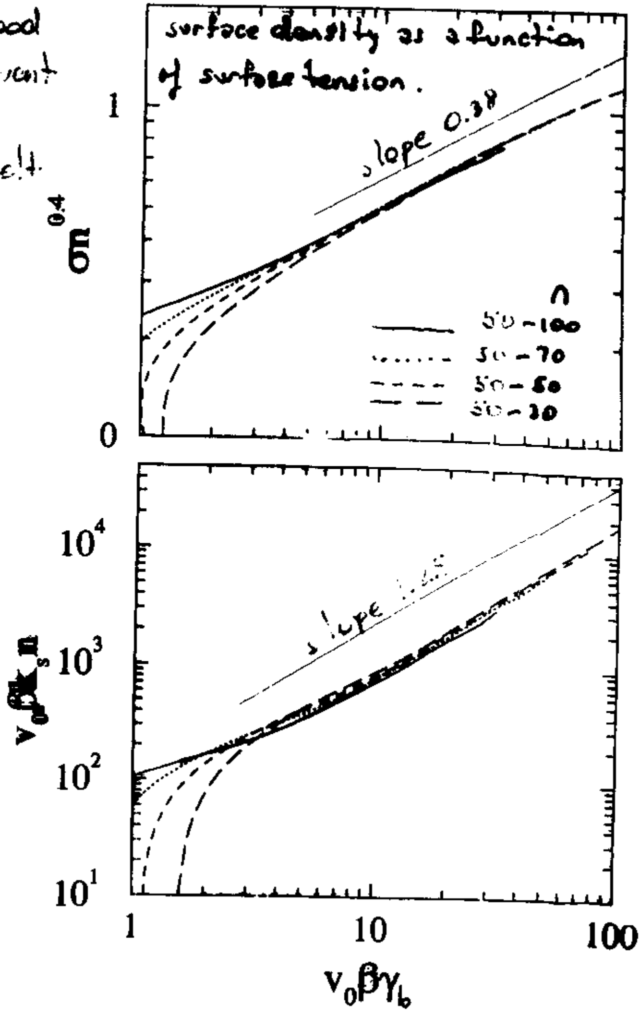


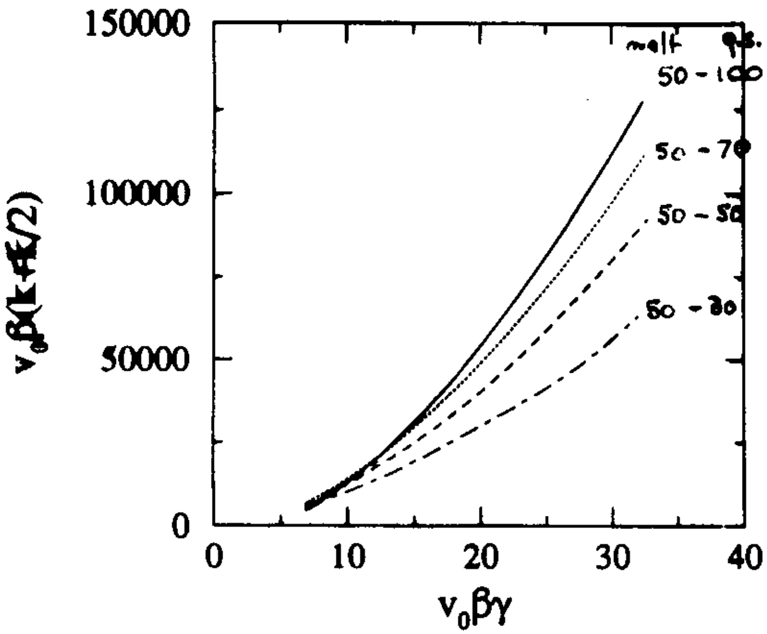


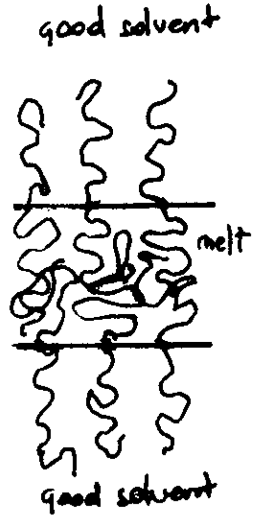


$k_s \propto \left(\frac{a^4}{\Theta a^2}\right)$

stretching constant

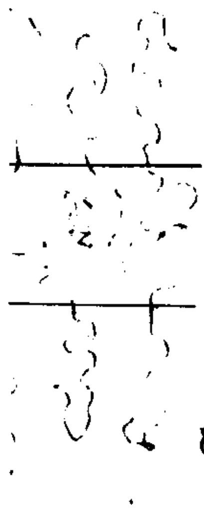


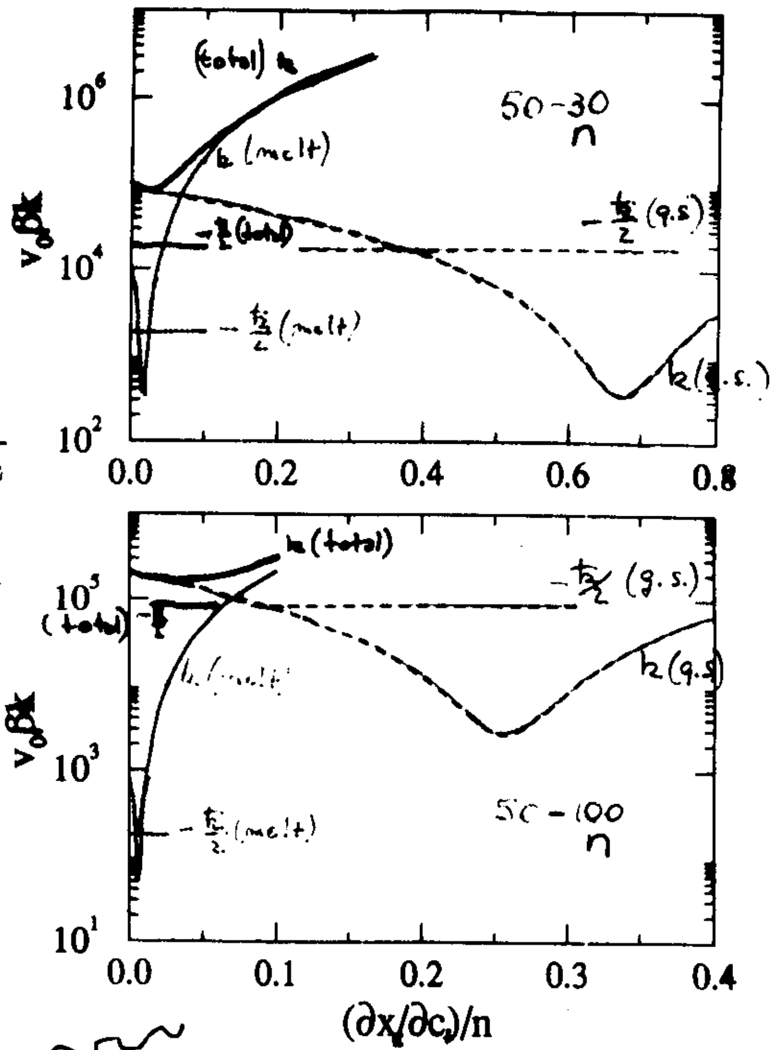


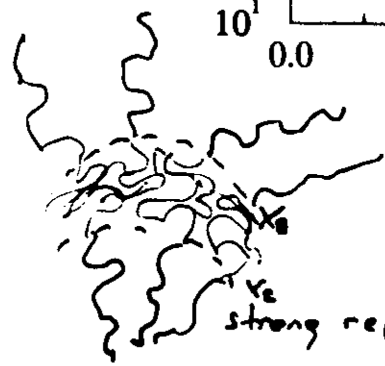


$= \frac{1}{2}\left(k+\frac{\bar{k}}{2}\right)c^2$ (spherical deformation)

$k+\frac{\bar{k}}{2} > 0$ due to strong q.s. chain repulsions upon deformation.







strong repulsions released by large $\frac{\partial x}{\partial c}$