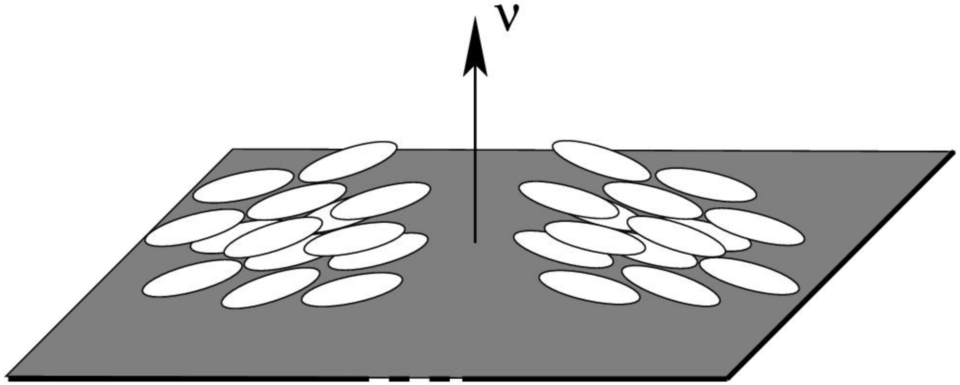
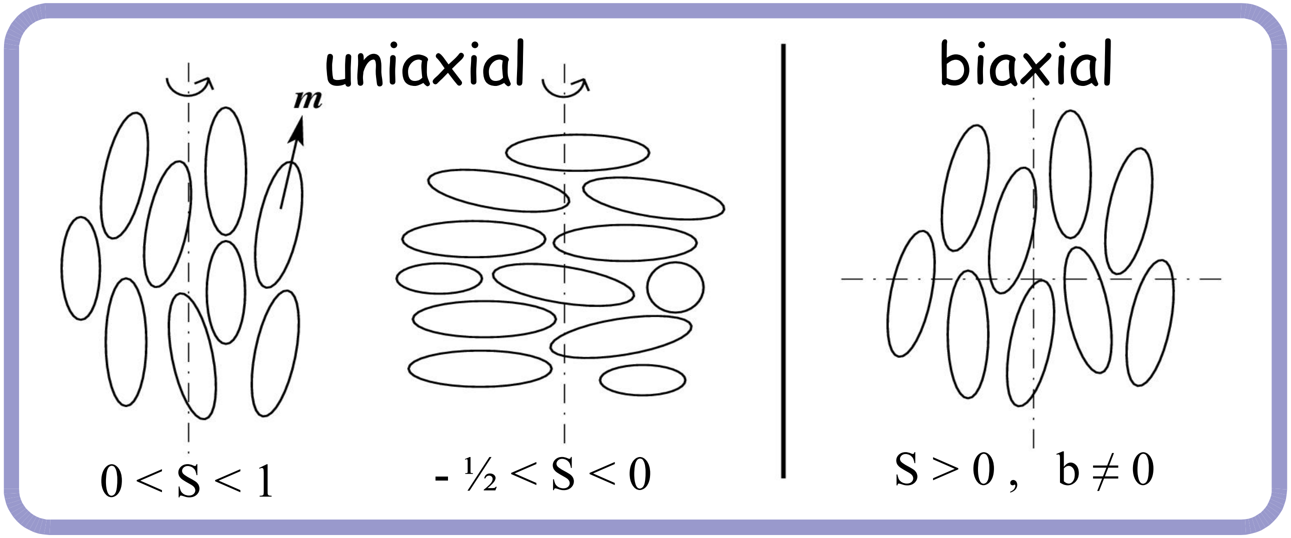
SMMM, Cortona (2005)

Modeling planar degenerate anchoring and wetting

J.-B. Fournier & P. Galatola



Nematic order

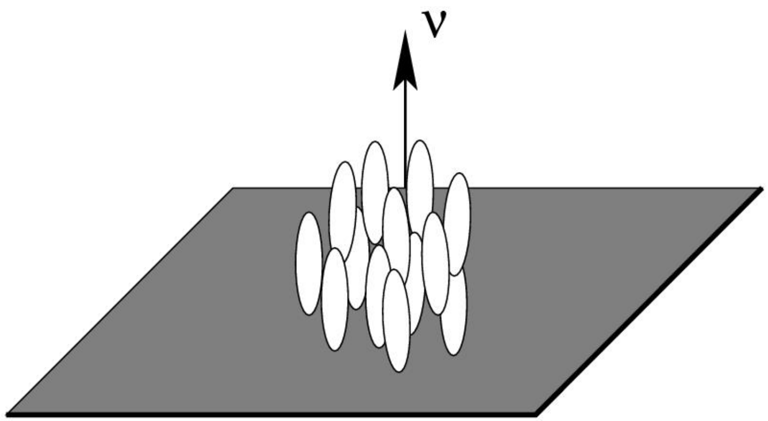


$$Q_{ij}(\boldsymbol{r}) = \langle m_i(\boldsymbol{r})\, m_j(\boldsymbol{r}) - \frac{1}{3}\delta_{ij}\rangle \;=\; \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix}_{\{\boldsymbol{e}_1,\boldsymbol{e}_2,\boldsymbol{e}_3\}}$$

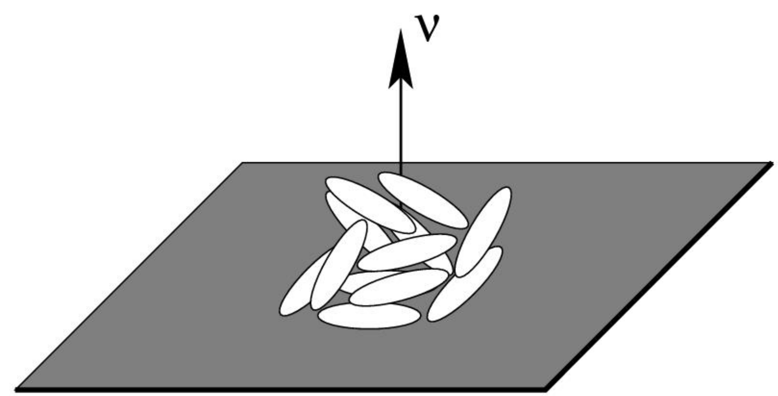
$$\alpha_1 + \alpha_2 + \alpha_3 = 0\,, \qquad |\alpha_1| \le |\alpha_2| \le |\alpha_3|\,.$$

- $\boldsymbol{e}_3 := \boldsymbol{n}$ defines the director,
- $\alpha_3 := \frac{2}{3}S$ defines S,
- $\{\alpha_1, \alpha_2\} = \{-\frac{1}{3}S(1-b), -\frac{1}{3}S(1+b)\}$ defines $0 \le b \le 1$.

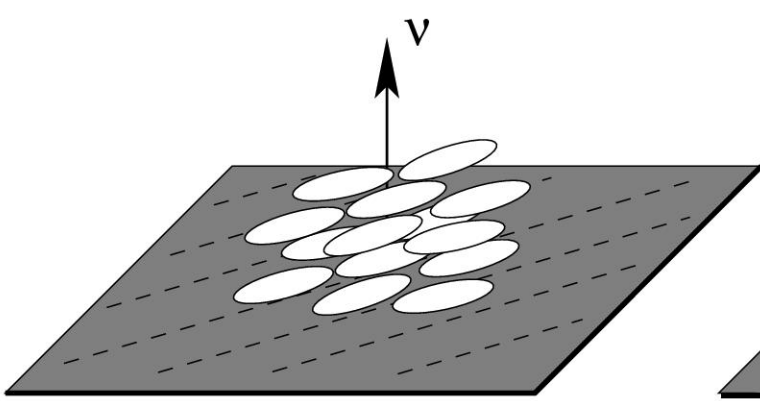
Anchoring



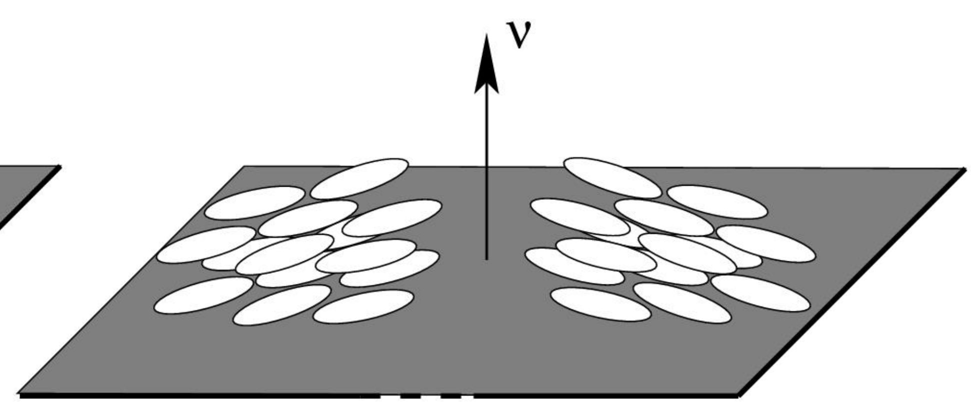
homeotropic (S > 0)



homeotropic (**S < 0**)

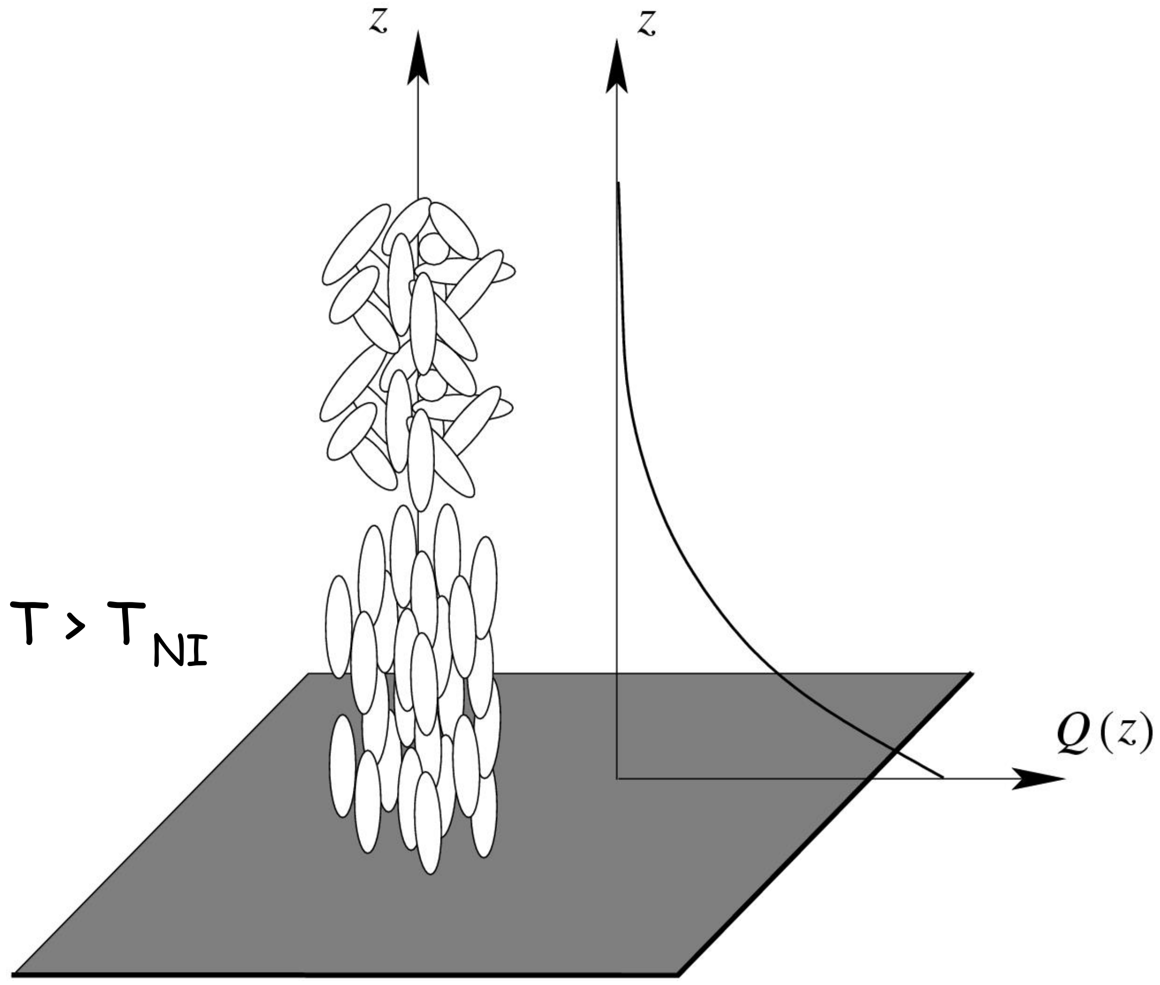


planar (S > 0)



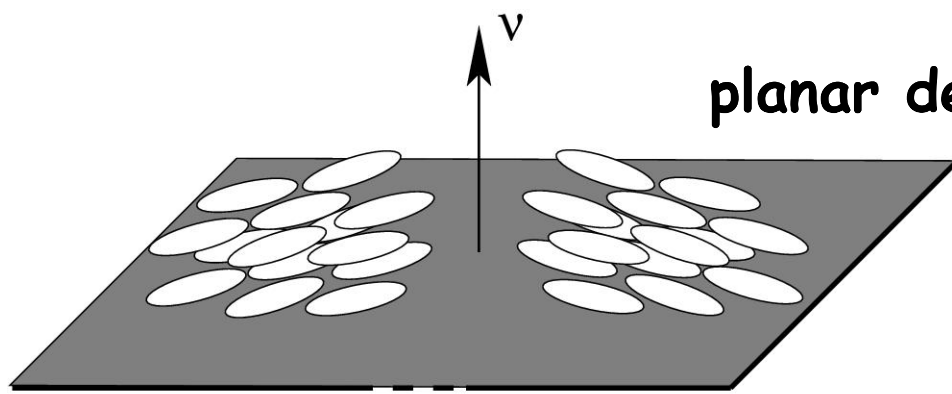
planar degenerate (S > 0)

Wetting



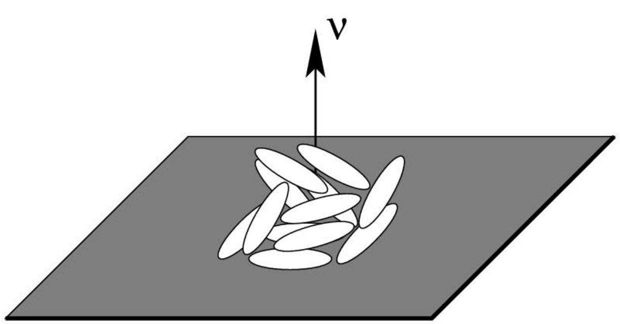
P. Sheng (1976) - K. Miyano (1979)

Model anchoring and wetting in this situation :



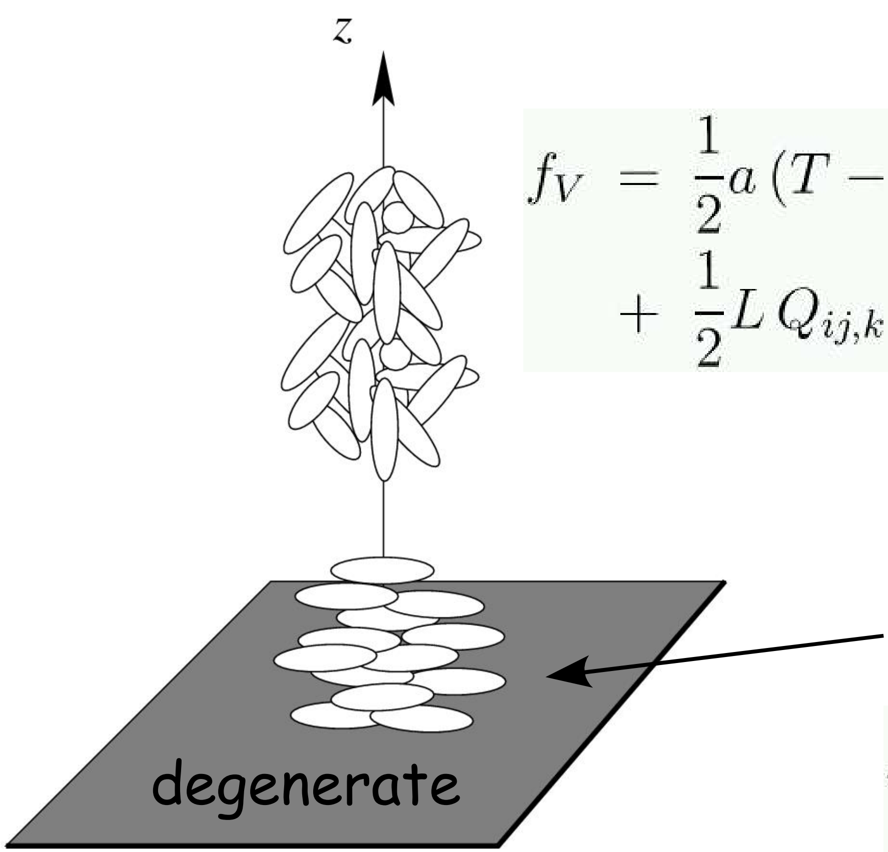
planar degenerate ($S > 0$)

NB. ≠ homeotropic with $S < 0$:



- Sluckin et al. (1985)
- Allender et al. (1997)
- Stark et al. (2005)

Free energies



$$f_V = \frac{1}{2}a\,(T - T^{\star})\,Q_{ij}\,Q_{ij} - \frac{1}{3}b\,Q_{ij}Q_{jk}\,Q_{ki} + \frac{1}{4}c\,\left(Q_{ij}\,Q_{ij}\right)^2 + \frac{1}{2}L\,Q_{ij,k}\,Q_{ij,k}$$

$$\cancel{f_S^{\mathrm{ND}} = \frac{1}{2}W\left(Q_{ij} - Q_{ij}^{(0)}\right)\left(Q_{ij} - Q_{ij}^{(0)}\right)}$$

$$\cancel{f_S^{(2)} = W_{11}\,\nu_i\,Q_{ij}\,\nu_j + W_{21}\,Q_{ij}\,Q_{ij} + W_{22}\,(\nu_i\,Q_{ij}\,\nu_j)^2 + W_{23}\,\nu_i\,Q_{ij}\,Q_{jk}\,\nu_k}$$

Surface potential favoring planar degenerate

Minimum: $Q_{ij} = S_0 \left(n_i\, n_j - \frac{1}{3}\delta_{ij} \right)$, $\forall \boldsymbol{n} \parallel$ surface

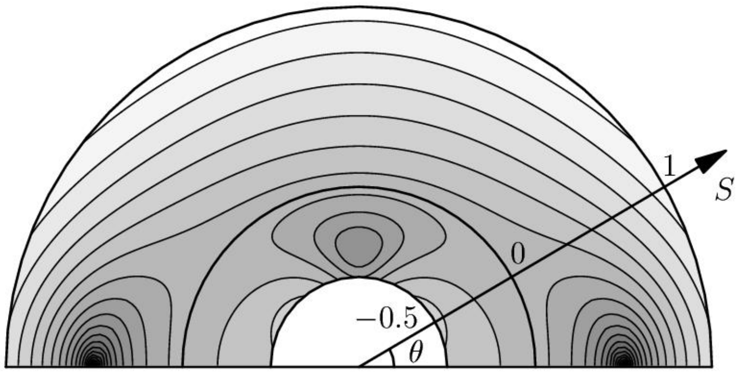
$$\boxed{\tilde{Q}_{ij} \;:=\; Q_{ij} + \tfrac{1}{3} S_0\, \delta_{ij}} \qquad \longrightarrow S_0\, n_i\, n_j$$

1. $\tilde{Q}_{ij} = \tilde{Q}^{\perp}_{ij} \;:=\; P_{ik}\, \tilde{Q}_{k\ell}\, P_{\ell j}$, where $P_{ij} = \delta_{ij} - \nu_i \nu_j$.

2. $\tilde{Q}_{ij}\, \tilde{Q}_{ij} = {S_0}^2$.

Surface potential

$$f_S = W_1 \left(\tilde{Q}_{ij} - \tilde{Q}^{\perp}_{ij}\right)\left(\tilde{Q}_{ij} - \tilde{Q}^{\perp}_{ij}\right) + W_2 \left(\tilde{Q}_{ij}\,\tilde{Q}_{ij} - {S_0}^2\right)^2$$



$$\begin{aligned} f_S \;&=\; W_1 \left[2\left(Q_{xz}^2 + Q_{yz}^2\right) + \left(Q_{xx} + Q_{yy} - \frac{S_0}{3}\right)^2\right] \\ &+\; 4\,W_2 \left(Q_{xx}^2 + Q_{yy}^2 + Q_{xx}\,Q_{yy} + Q_{xy}^2 + Q_{xz}^2 + Q_{yz}^2 - \frac{{S_0}^2}{3}\right)^2 \end{aligned}$$

Minimization problem

transition
$\tau=1$

$$\mathsf{Q}(z) = \begin{pmatrix} -\alpha(z)-\beta(z) & 0 & 0 \\ 0 & \alpha(z) & \gamma(z) \\ 0 & \gamma(z) & \beta(z) \end{pmatrix}$$

bulk :

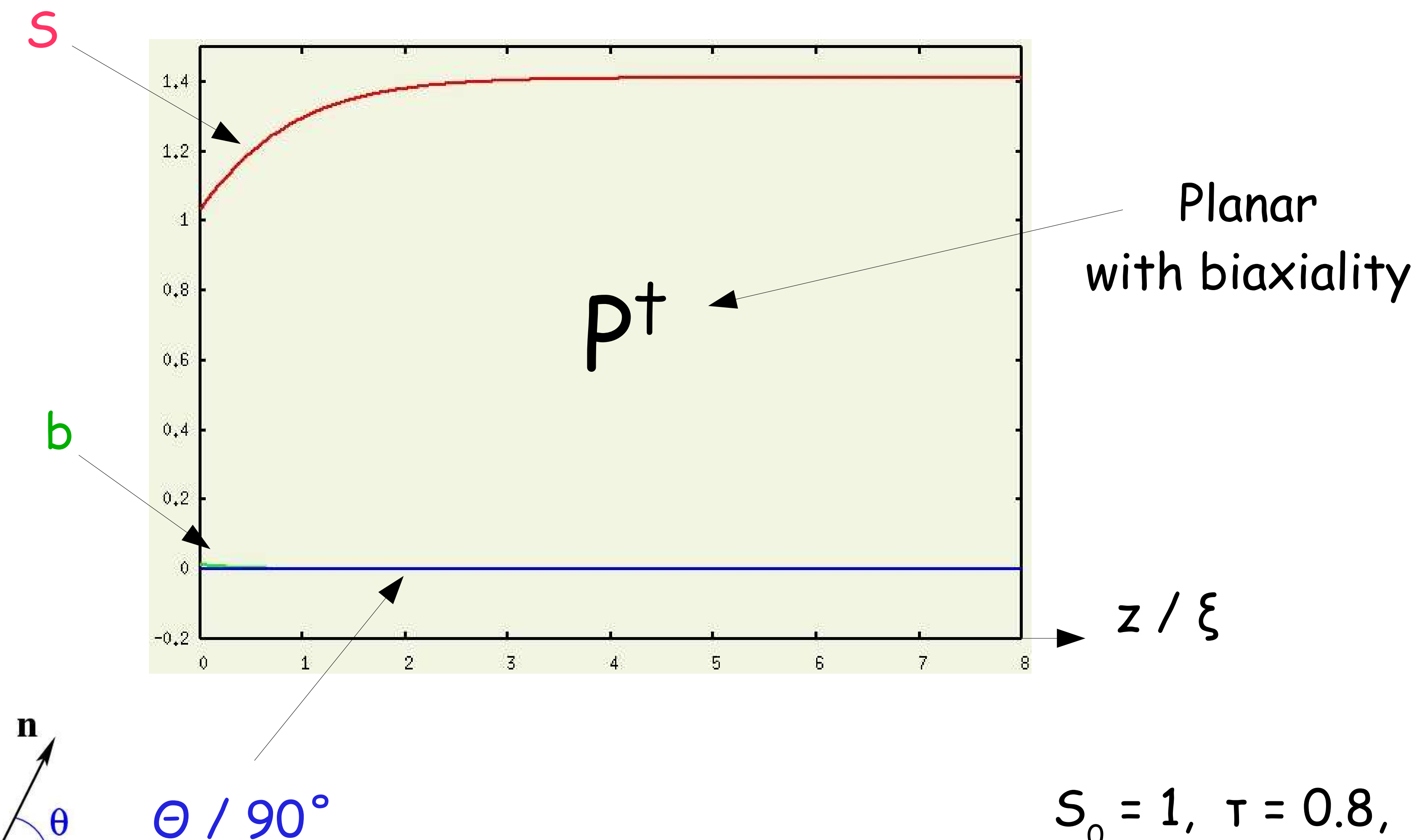
$$\begin{aligned}
\frac{d^2\alpha}{dz^2} &= \tau\alpha - \sqrt{6}\left(\alpha^2 - 2\beta^2 + \gamma^2 - 2\alpha\beta\right) + 4\alpha\left(\alpha^2+\beta^2+\gamma^2+\alpha\beta\right), \\
\frac{d^2\beta}{dz^2} &= \tau\beta - \sqrt{6}\left(\beta^2 - 2\alpha^2 + \gamma^2 - 2\alpha\beta\right) + 4\beta\left(\alpha^2+\beta^2+\gamma^2+\alpha\beta\right), \\
\frac{d^2\gamma}{dz^2} &= \gamma\left[\tau - 3\sqrt{6}\left(\alpha+\beta\right) + 4\left(\alpha^2+\beta^2+\gamma^2+\alpha\beta\right)\right],
\end{aligned}$$

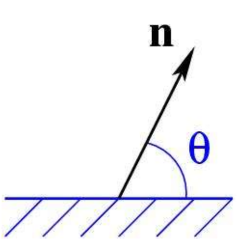
boundary :

$$\begin{aligned}
\left.\frac{d\alpha}{dz}\right|_{z=0} &= \frac{8}{3}w_2\,\alpha\left[3\left(\alpha^2+\beta^2+\gamma^2+\alpha\beta\right) - s_0^2\right] - \frac{2}{9}w_1\left(3\beta+s_0\right), \\
\left.\frac{d\beta}{dz}\right|_{z=0} &= \frac{8}{3}w_2\,\beta\left[3\left(\alpha^2+\beta^2+\gamma^2+\alpha\,\beta\right) - s_0^2\right] + \frac{4}{9}w_1\left(3\beta+s_0\right), \\
\left.\frac{d\gamma}{dz}\right|_{z=0} &= \gamma\left[\frac{8}{3}w_2\left[3\left(\alpha^2+\beta^2+\gamma^2+\alpha\,\beta\right) - s_0^2\right] + \frac{6}{3}w_1\right],
\end{aligned}$$

$$\left.\frac{d\alpha}{dz}\right|_{z=\infty} = \left.\frac{d\beta}{dz}\right|_{z=\infty} = \left.\frac{d\gamma}{dz}\right|_{z=\infty} = 0.$$

In the nematic phase

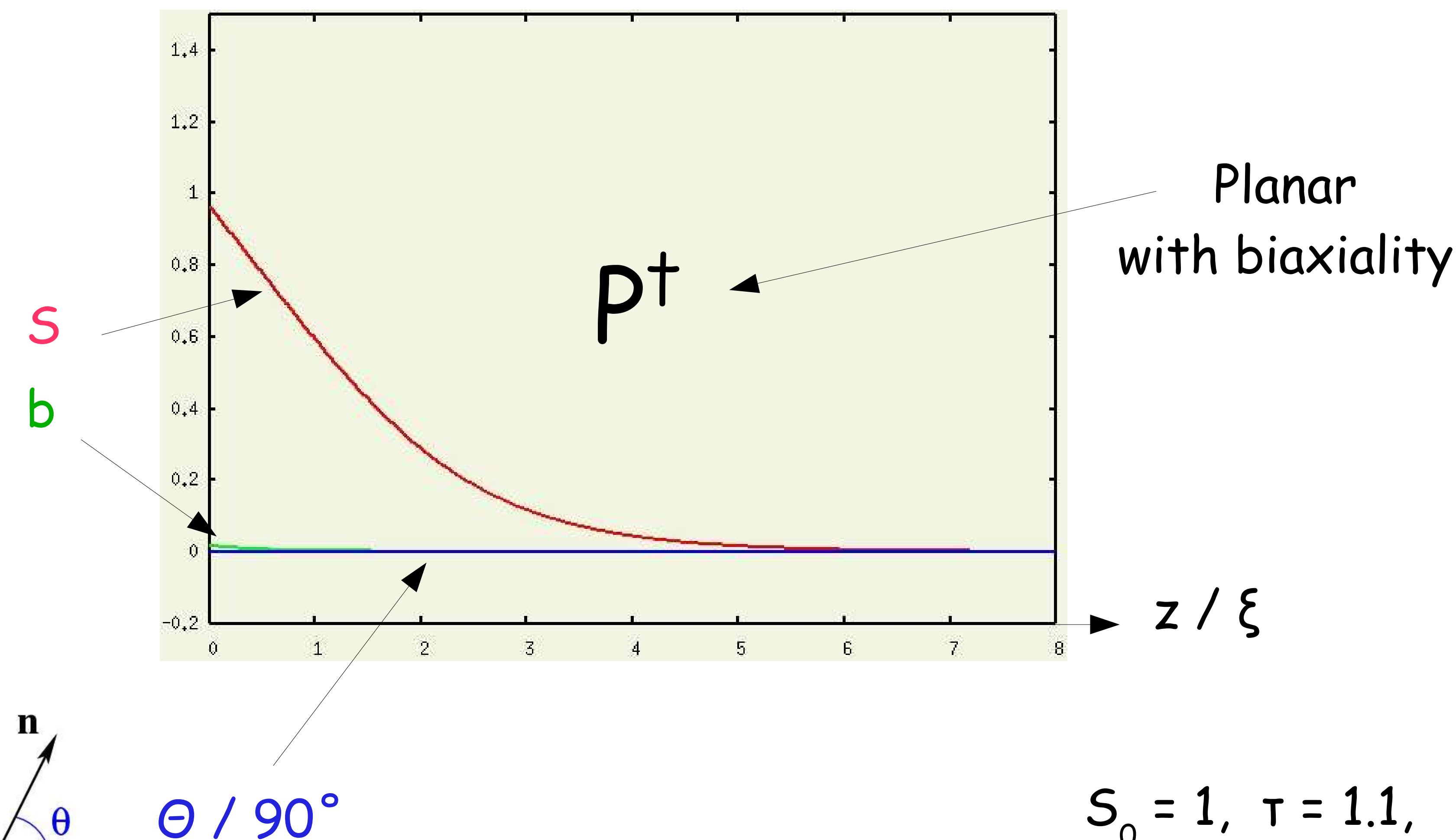


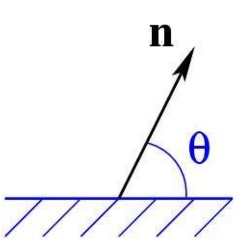


$S_0 = 1, \ \tau = 0.8,$

$w_1 = w_2 = 2$

In the isotropic phase
- **large** coupling -



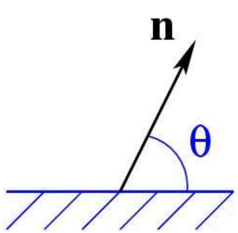


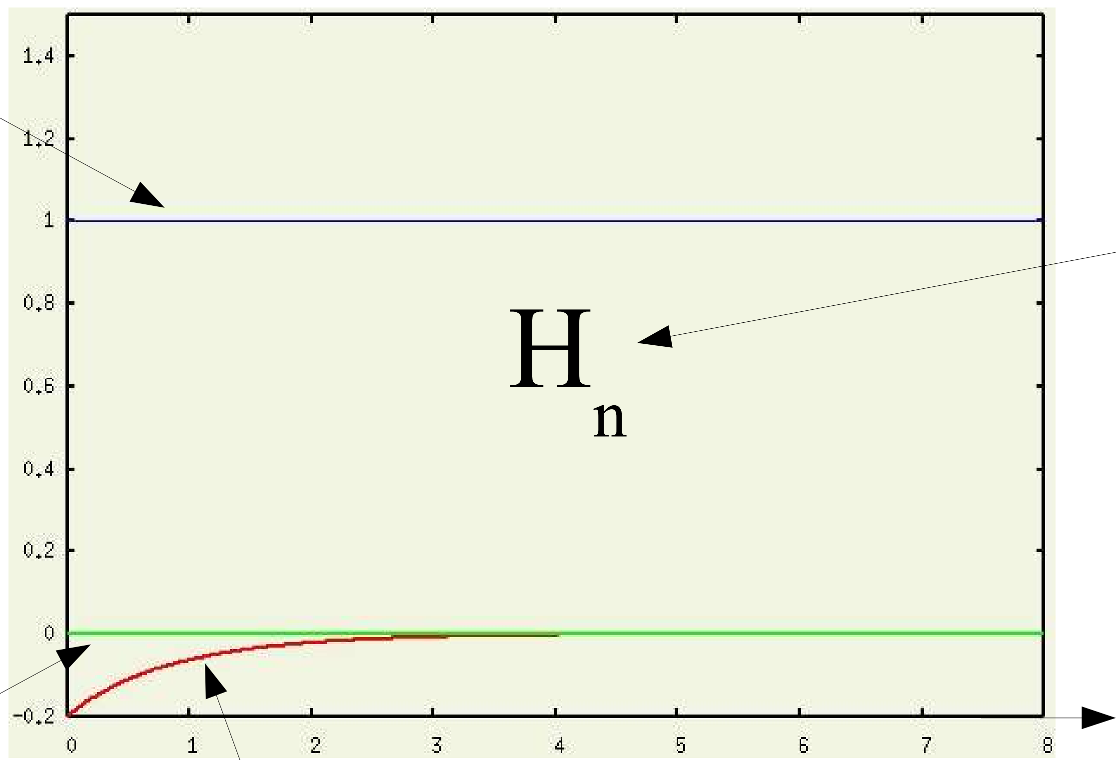
$S_0 = 1, \ \tau = 1.1,$

$w_1 = w_2 = 2$

In the isotropic phase
- **weak** coupling -

Θ / 90°





Homeotropic negative

z / ξ

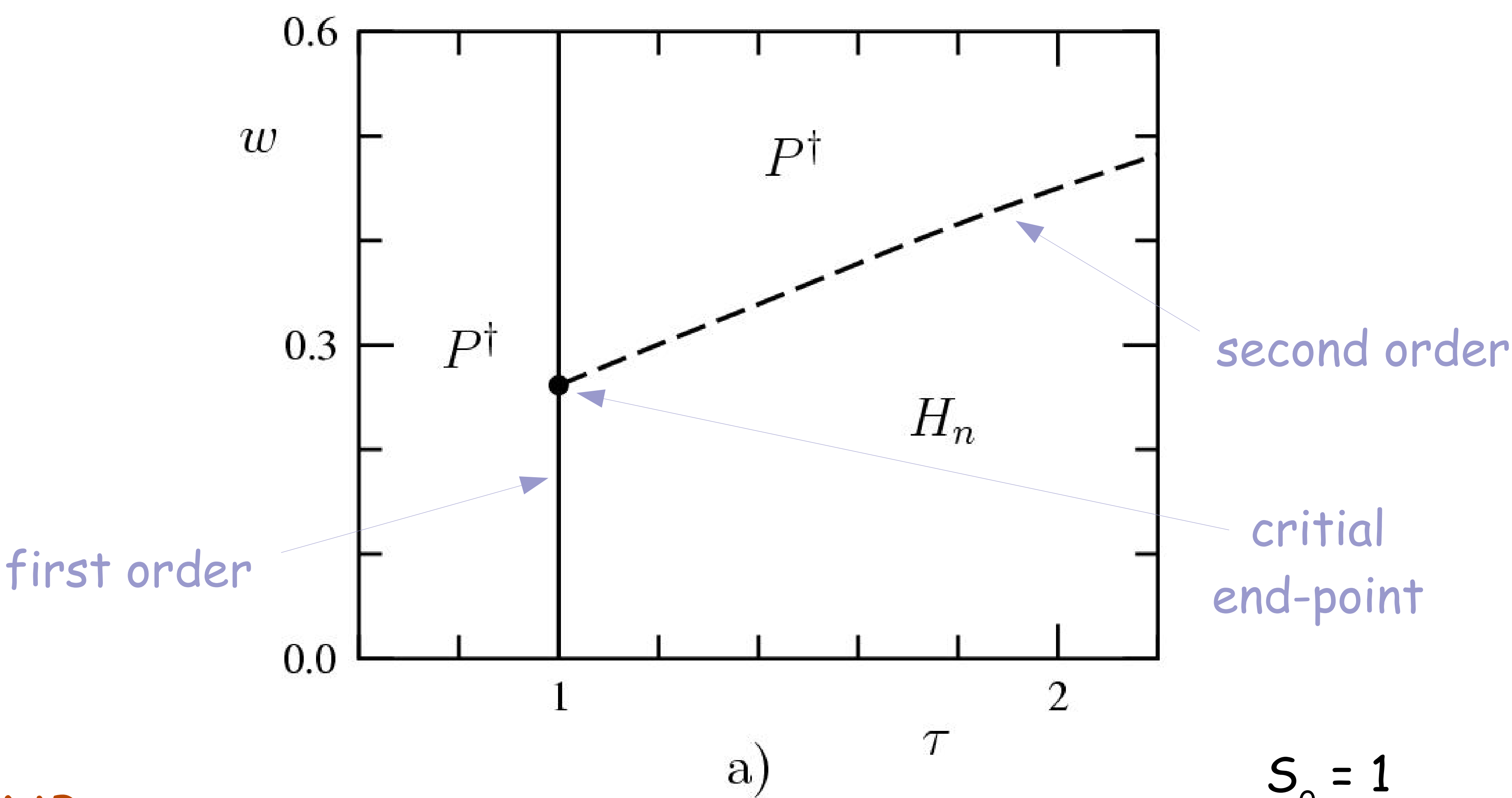
b = 0

S

$S_0 = 1$, $\tau = 1.1$,

$w_1 = w_2 = 0.26$

Phase diagram

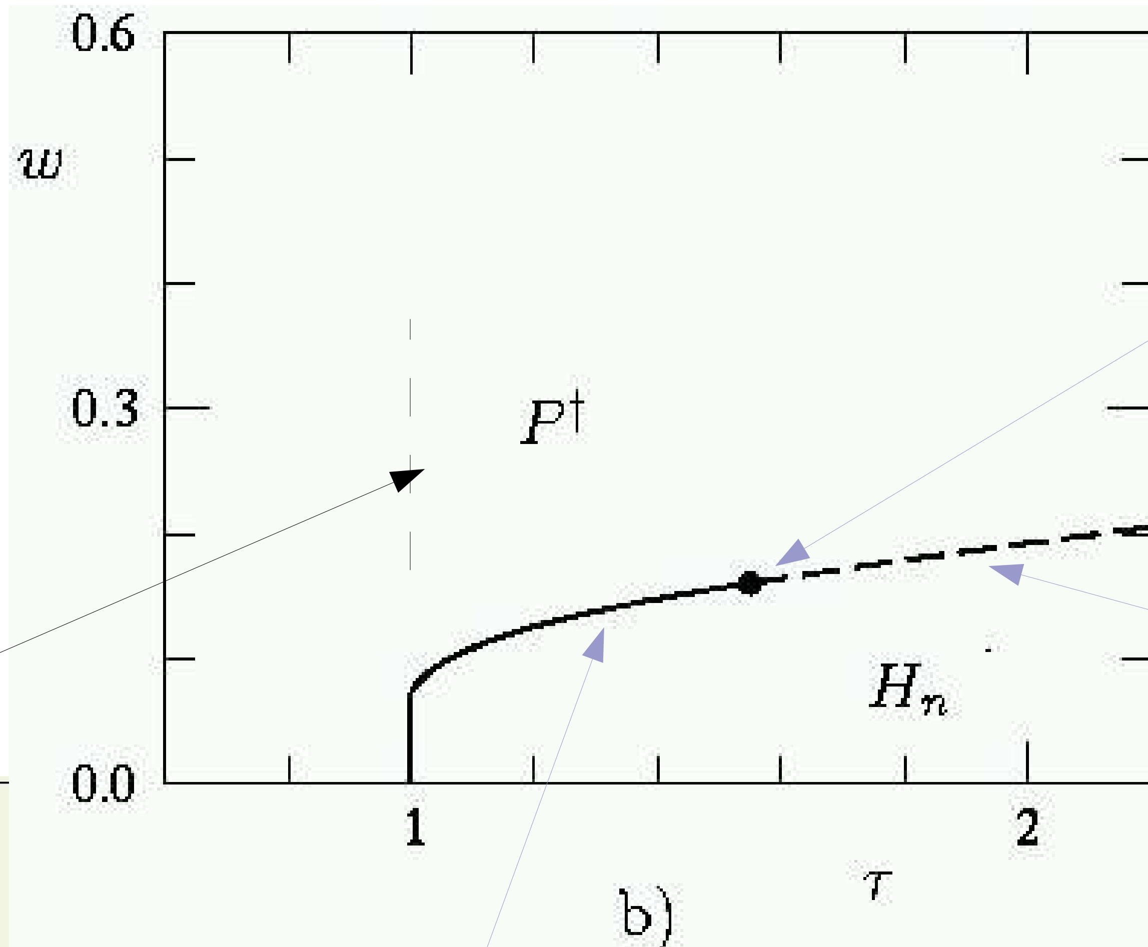


NB. $s_0 < s_{tr}$

$S_0 = 1$

$w_1 = w_2 = w$

Phase diagram: for $s_0 > s_{tr}$

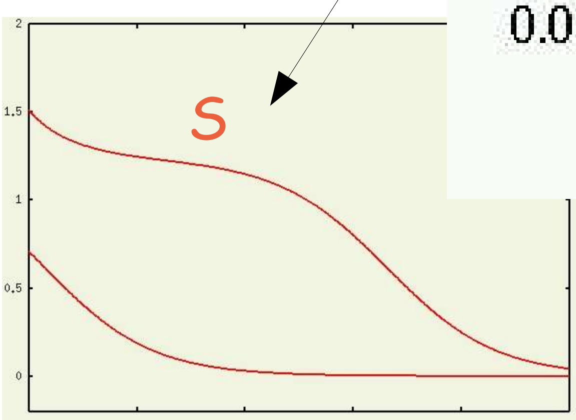


tricritial point

second order

first order

complete wetting



z

$S_0 = 1.5$

$w_1 = w_2 = w$

Conclusions

- Compatible with experiments of Tarczon and Miyano (1980) observing pretransitional uniaxial negative birefringence with optical axis perpendicular to the surface (i.e., H_n) for MBBA in contact with silane-treated substrate, *giving planar degenerate anchoring in the nematic phase.*

- Useful tool to study anchoring/wetting problems with degenerate planar anchoring (defects around particles, capillary interactions, colloids suspensions, etc.)

- Liquid emulsions as colloids?

Detail of the second order transition