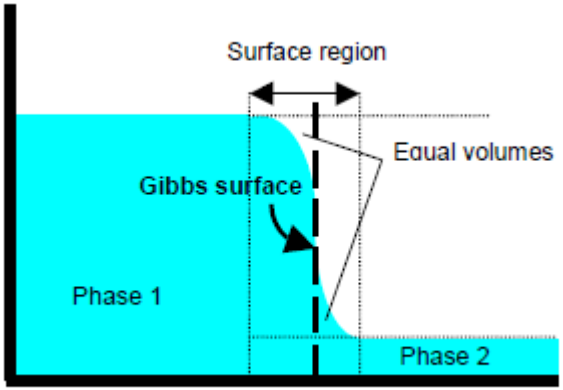
Molecular-statistical theory of surface Anchoring of nematic LCs. Fundamental problems.

M.A.Osipov
Department of Mathematics and Statistics, University of Strathclyde, 26 Richmond Str. Glasgow

1. **Existing theory**
2. **Speculations**

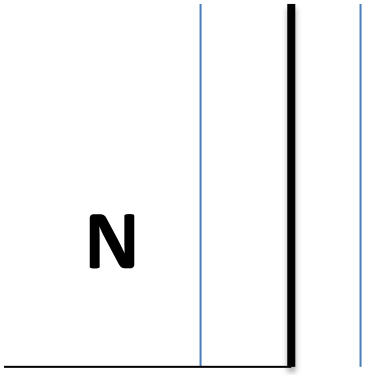
Different types of surfaces

Gibbs surface



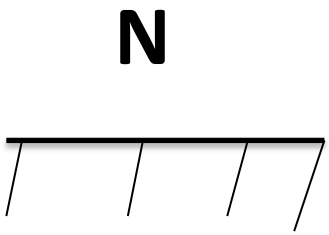
$$\rho_1 V_1 + \rho_2 V_2 = N$$

Nematic-Isotropic interface

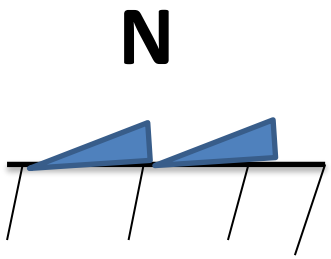


$$LS = \int S(z)dz --?$$

Sharp surface



Rough surface



Molecular theory of surface anchoring of nematics

Sharp surface

N

Crystalline, Amorphous and rough surfaces

Some relevant works

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P. I. C. Teixeira and T. J. Sluckin, J. Chem. Phys., 1992, 97, 1498–

M.A.Osipov and S.Hess, J. Chern. Phys. 99, 4181 (1993).

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Barbero, G.; Evangelista, L. R. Adsorption Phenomena and Anchoring Energy in Nematic LCs; Taylor & Francis, 2006

Atomistic simulations

Pizzirusso, A.; Berardi, R.; Muccioli, L.; Ricci, M.; Zannoni, C. Chem. Sci. **2012**, 3, 573

O.M. Roscioni, L.Muccioli, R.G. Della Valle, A. Pizzirusso, M. Ricci, and C. Zannoni. Langmuir, 2013

Density functional approach

Free energy functional $F = \Phi + H$

$$\Phi = kT \int \rho(\mathbf{x}) [\ln \rho(\mathbf{x}) \Lambda + 1] d\mathbf{x}.$$

$$\delta^2 H / \delta\rho(\mathbf{x}_1) \delta\rho(\mathbf{x}_2) = -kT C_2(\mathbf{x}_1, \mathbf{x}_2)$$

Expansion around the isotropic phase

$$\Delta H/kT = -(1/2) \int C_2(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2) \delta\rho(\mathbf{r}_1, \mathbf{u}_1)$$

$$\times \delta\rho(\mathbf{r}_2, \mathbf{u}_2) d^2\mathbf{u}_1 \, d^2\mathbf{u}_2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2,$$

$$\delta\rho(\mathbf{r}, \mathbf{u}) = \rho(\mathbf{r}, \mathbf{u}) - (4\pi)^{-1} \rho_0(r)$$

The difference between the one-particle densities in N and I phases

Landau-de Gennes theory

$$\Delta F = \int_0^\infty dz\{f_G[\dot{Q}(z)] + f_L[Q(z)]\} + f_s(Q_0)$$

Bulk free energy

$$f_L(Q) = A\ \mathrm{Tr}\ Q^2 - B\ \mathrm{Tr}\ Q^3 + C(\mathrm{Tr}\ Q^2)^2$$

Gradient terms

$$f_G(\dot{Q}) = (1/2)\,L_1\ \mathrm{Tr}\ \dot{Q}^2 + (1/2)\,L_2(\mathbf{k}\cdot\dot{Q}\cdot\mathbf{k})^2$$

Surface free energy

$$f_s(Q_0) = c_1\mathbf{k}\cdot Q_0\cdot\mathbf{k} + c_2\ \mathrm{Tr}\ Q_0^2 + c_3(\mathbf{k}\cdot Q_0\cdot\mathbf{k})^2 + c_4\mathbf{k}\cdot Q_0^2\cdot\mathbf{k}.$$

Г. J. Sluckin and A. Poniewierski, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, Chichester, 1986), Chap. 5.

L-dG theory from the density functional approach

$$\Delta H/kT = -(1/2)\int C_2(\mathbf{r}_{12},\mathbf{u}_1,\mathbf{u}_2)\delta\rho(\mathbf{r}_1,\mathbf{u}_1)$$

$$\times\delta\rho(\mathbf{r}_2,\mathbf{u}_2)d^2\mathbf{u}_1\, d^2\mathbf{u}_2\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2,$$

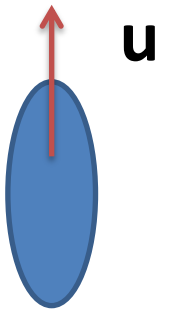
Gradient expansion of the orientational density

$$\rho(\mathbf{r}_2,\mathbf{u}_2) = \rho(\mathbf{r}_1,\mathbf{u}_2) + (\mathbf{r}_{12}\nabla)\rho(\mathbf{r}_1,\mathbf{u}_2) + \cdots$$

Q-tensor expansion to the second order

$$\rho(\mathbf{r},\mathbf{u}) = (4\pi)^{-1}\rho_0(z)\,[1 + (15/2)\phi_{\mu\nu}Q_{\mu\nu}(z) + \cdots]$$

$$\phi_{\mu\nu} = u_\mu u_\nu - (1/3)\delta_{\mu\nu}$$ **Molecular tensor**



L-dG theory from the density functional approach

$$\Delta F/kT = \int_0^\infty dz_1 [A Q_{\alpha\beta}(z) Q_{\alpha\beta}(z)] + R_0 Q_{zz} \left(\frac{d\rho_0}{dz}\right)^2$$
$$+ G_{\alpha\beta}(z) Q_{\alpha\beta} + H_{\alpha\beta\gamma\delta}(z) Q_{\alpha\beta} Q_{\gamma\delta}$$
$$+ \tfrac{1}{2} L_1 \dot{Q}_{\alpha\beta} \dot{Q}_{\alpha\beta} + \tfrac{1}{2} L_2 \dot{Q}_{z\alpha} \dot{Q}_{z\beta})$$

Surface energy tensors

$$G_{\alpha\beta}(z) = \frac{15}{4} \rho_0^2 \int_z^\infty dz_{12} \int dx_{12}\, dy_{12}\, d^2\mathbf{u}_1 d^2\mathbf{u}_2$$
$$\times C_2(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2)\, (1/2)\, (\phi_{\alpha\beta}^{(1)} + \phi_{\alpha\beta}^{(2)}),$$
$$H_{\alpha\beta\gamma\delta}(z) = \frac{1}{2} \left(\frac{15}{2}\right)^2 \rho_0^2 \int_z^\infty dz_{12} \int dx_{12}\, dy_{12}\, d^2\mathbf{u}_1 d^2\mathbf{u}_2$$
$$\times C_2(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2)\, (1/2)\, \phi_{\alpha\beta}^{(1)} \phi_{\gamma\delta}^{(2)}$$

Elastic constants

$$L_1 = L_0 - \tfrac{1}{3} L_2,$$

$$L_0 = \tfrac{1}{2}\rho_0^2 \langle\langle r^2 \phi_{\alpha\beta}^{(1)} \phi_{\alpha\beta}^{(2)} \rangle\rangle,$$

$$L_2 = \frac{36}{7}\, \rho_0^2 \langle\langle (r_\mu r_\nu - \tfrac{1}{3}\delta_{\mu\nu}) \phi_{\alpha\mu}^{(1)} \phi_{\alpha\nu}^{(2)} \rangle\rangle,$$

$$\langle\langle (\cdots) \rangle\rangle = \left(\frac{15}{8\pi}\right)^{-2} \int d^2\mathbf{u}_1\, d^2\mathbf{u}_2\, d^3\mathbf{r} (\cdots) C_2(\mathbf{u}_1, \mathbf{r}, \mathbf{u}_2)$$

Approximation 1
Direct corr. Function is very short ranged

$$Q(z) = Q^0$$ **Surface order parameter**

$$f_s = \bar{G}_{\alpha\beta} Q^0_{\alpha\beta} + \bar{H}_{\alpha\beta\gamma\delta} Q^0_{\alpha\beta} Q^0_{\gamma\delta}$$ **Surface free energy**

$$\bar{H}_{\alpha\beta\gamma\delta} = \frac{1}{2}\left(\frac{15}{2}\right)^2 \rho_0^2 \int_0^\infty dz \int_z^\infty dz_{12} \int dx_{12}\, dy_{12}\, d^2\mathbf{u}_1$$

$$\times d^2\mathbf{u}_2 C_2(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2)\,(1/2)\,\phi^{(1)}_{\alpha\beta}\phi^{(2)}_{\gamma\delta}$$

Approximation 2
Direct corr. funct. Is independent of z

$$\int_0^\infty\int_0^\infty C_2(z_{12})dz_1 dz_2 = \int_0^\infty\int_{-z}^\infty C_2(z_{12})dz_{12}dz = -\int_0^\infty z_{12}C_2(z_{12})dz_{12} + bulk$$

Surface free energy

$$f_s(Q_0)=c_1\mathbf{k}\cdot Q_0\cdot\mathbf{k}+c_2\ \mathrm{Tr}\ Q_0^2+c_3(\mathbf{k}\cdot Q_0\cdot\mathbf{k})^2 +c_4\mathbf{k}\cdot Q_0^2\cdot\mathbf{k}.$$

$$f_s=\bar{G}_{\alpha\beta}Q^0_{\alpha\beta}+\bar{H}_{\alpha\beta\gamma\delta}Q^0_{\alpha\beta}Q^0_{\gamma\delta}$$

General form

$$H_{\alpha\beta\gamma\delta}=c_2\tfrac{1}{22}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})+c_3k_\alpha k_\beta k_\gamma k_\delta+c_4\tfrac{1}{44}(k_\alpha k_\gamma\delta_{\beta\delta} +k_\alpha k_\delta\delta_{\gamma\beta}+k_\gamma k_\beta\delta_{\delta\alpha}+k_\delta k_\beta\delta_{\gamma\alpha}).$$

In terms of orthogonal tensors

$$G_{\alpha\beta}=c_1k_\alpha{*}k_\beta,$$

$$H_{\alpha\beta\gamma\delta}=a_4k_\alpha{*}k_\beta{*}k_\gamma{*}k_\delta+a_3D_{\alpha\beta,\gamma\delta}+a_2C_{\alpha\beta,\gamma\delta},$$

$$D_{\alpha\beta,\gamma\delta}=-k_\alpha{*}k_\beta\delta_{\gamma\delta}-k_\gamma{*}k_\delta\delta_{\alpha\beta}+\tfrac{3}{4}(k_\alpha{*}k_\gamma\delta_{\beta\delta} +k_\alpha{*}k_\delta\delta_{\gamma\beta}+k_\gamma{*}k_\beta\delta_{\delta\alpha}+k_\delta{*}k_\beta\delta_{\gamma\alpha}),$$

$$C_{\alpha\beta,\gamma\delta}=\tfrac{1}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})-\tfrac{1}{3}\delta_{\alpha\beta}\delta_{\gamma\delta},$$

$$k_\alpha{*}k_\beta=k_\alpha k_\beta-\tfrac{1}{3}\delta_{\alpha\beta}.$$

General expressions for the coefficients

$$a_2=\frac{15}{4}\langle\langle[(\mathbf{u}_1\mathbf{u}_2)^2-\tfrac{1}{3}]\rangle\rangle,$$

$$a_3=\frac{75}{14}\left\langle\left\langle\frac{9}{2}(\mathbf{u}_1\mathbf{u}_2)[(\mathbf{u}_1\mathbf{k})(\mathbf{u}_2\mathbf{k})-\tfrac{1}{3}(\mathbf{u}_1\mathbf{u}_2)]\right.\right.$$

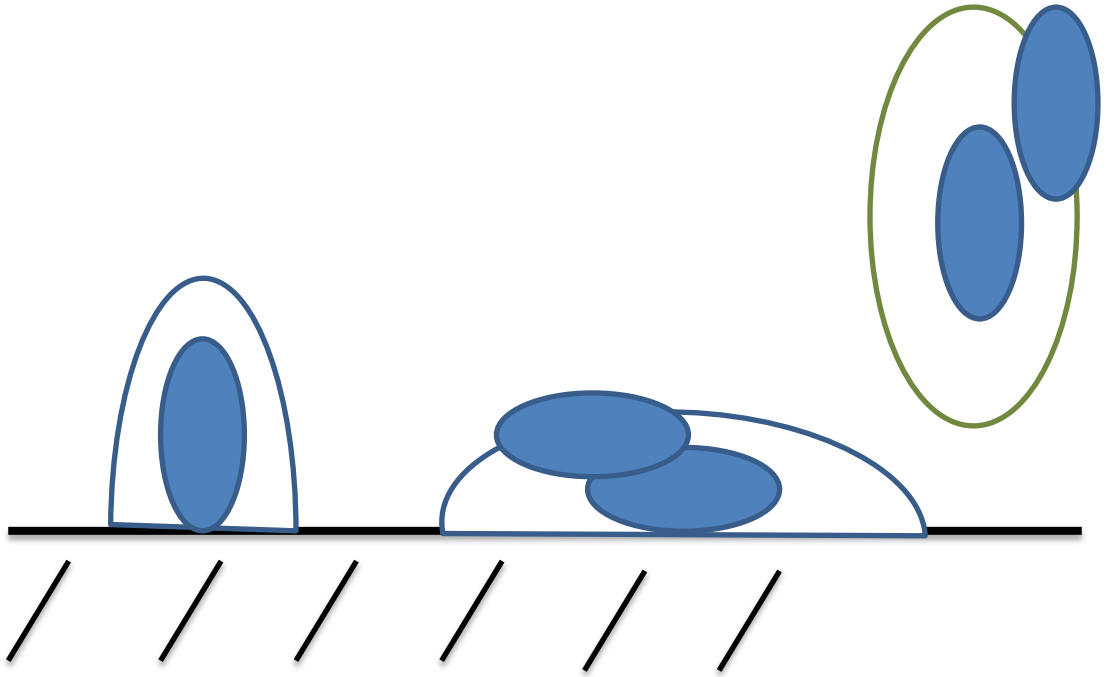
$$\left.\left.-P_2(\mathbf{u}_1\mathbf{k})-P_2(\mathbf{u}_2\mathbf{k})\right\rangle\right\rangle,$$

And so on….

$$\langle\langle\cdots\rangle\rangle=(4\pi)^{-2}\rho_0^2\int d^2\mathbf{u}_1\,d^2\mathbf{u}_2\,d^3\mathbf{r}(\cdots)$$

$$\times C_2(\mathbf{u}_1,\mathbf{r},\mathbf{u}_2)(\mathbf{rk})[1+\mathrm{sign}(\mathbf{rk})].$$

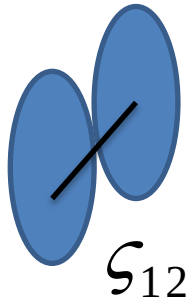
Origin of the surface anchoring



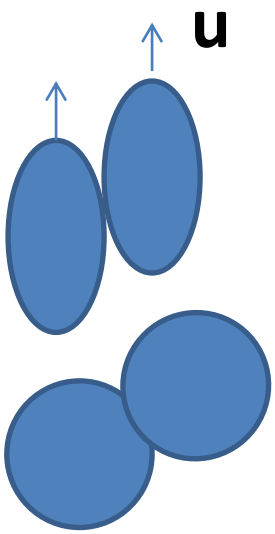
Generalised mean-field approximation.

$$C_2(1,2) = \theta(r_{12} - \varsigma_{12})V(1,2) + kT\lambda(\rho)[\theta(r_{12} - \varsigma_{12}) - 1]$$

Attraction repulsion



Perfect local order of ellipsoidal molecules



$$C_2(\mathbf{u}_1,\mathbf{r}_{12},\mathbf{u}_2)=4\pi C_2^0(\mathbf{r}_{12},\mathbf{u}_1)\delta(\mathbf{u}_1-\mathbf{u}_2)+\text{const},$$

Ornsrein-Zernike equation

$$h_2(1,2)=C_2(1,2)+\rho\int h_2(1,3)C_2(2,3)\,f_1(3)d(3)$$

$h_2(1,2)$ - **Pair correlation function**

Affine transformation. Mapping onto the sphere fluid

$$C^0(\mathbf{u},\mathbf{r})=C_{\text{ref}}(\mathbf{r}^A) \qquad r_\mu^A=A_{\mu\nu}^{1/2}r_\nu,$$

$$A_{\mu\nu}=Q^{2/3}[\delta_{\mu\nu}+(Q^{-2}-1)u_\mu u_\nu],$$

$$A_{\mu\nu}^{1/2}=Q^{1/3}[\delta_{\mu\nu}+(Q^{-1}-1)u_\mu u_\nu].$$

Maps ellipsoids onto spheres

$$Q=L/D$$

Anchoring energy

$$f_s(Q_0) = c_1 \mathbf{k}\cdot Q_0\cdot \mathbf{k} + c_2 \,\mathrm{Tr}\, Q_0^2 + c_3(\mathbf{k}\cdot Q_0\cdot \mathbf{k})^2 + c_4 \mathbf{k}\cdot Q_0^2\cdot \mathbf{k}.$$

$$c_2 = a_2 + \frac{2}{35}c_3; c_4 = \frac{3}{4}a_3 - \frac{4}{7}c_3.$$

$$Q = L/D$$

$$a_2 = \frac{15\pi}{16}\rho_0^2 C_0 Q^{2/3}\left(1 + \frac{\ln 2Q^2}{2Q^2}\right),$$

$$a_3 = \frac{75\pi}{28}\rho_0^2 C_0 Q^{2/3}\left(1 - \frac{\ln 2Q^2}{2Q^2}\right),$$

$$c_3 = \frac{15\pi}{16}\rho_0^2 C_0 Q^{2/3}\frac{25}{8}\left(-1 + \frac{9}{2}\frac{\ln 2Q^2}{Q^2}\right).$$

$$c_3 << c_2, c_4$$

$$C_0 = \int_0^\infty d\mathbf{r}\, r C_{\mathrm{ref}}(r),$$

No biaxial order at the surface

Anchoring energy

$$f_s = w_2 P_2(\cos\omega) + w_4 P_4(\cos\omega),$$

$$w_2 = \tfrac{2}{3}(c_1 S + a_3 S^2),$$

$$w_4 = \frac{8}{35} c_3 S^2,$$

$$\frac{w_4}{w_2} = \frac{[9(\ln 2Q^2/2Q^2) - 1]S}{5 + 3S} \leqslant 3 \cdot 10^{-2}$$

$w_2 > 0$ **Planar orientation**

$w_2 < 0$ **Homeotropic orientation**

Extremely short range direct correlation function

Free Energy
= Bulk free energy + Gradient terms + Gibbs surface energy

Surface values are boundary conditions in Landau-de Gennes Theory

The same in the Mean Field theory with short range interactions

Very strong anchoring

$$w \propto 10\rho^2 C_0 \left(L/D\right)^{2/3} S \propto (10^{-3} - 10^{-2})\, Jm^{-2}$$

Estimates of the anchoring strength

Semi microscopic (de Gennes) $V_{anis} L^{-2} \propto 5\,10^{-3}\,Jm^{-2}$

Macro-Total surface energy (E.Kats,) $\rho c^2 L \propto 10^{-1}\,Jm^{-2}$

Elasticity based $K / L \propto 3\,10^{-3}\,Jm^{-2}$

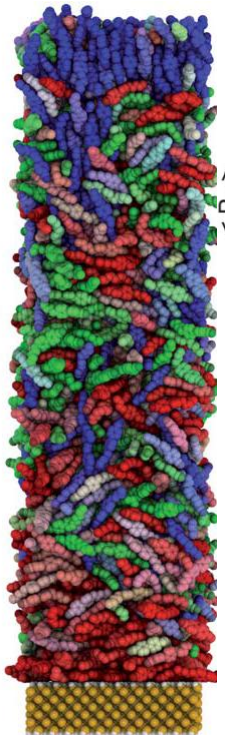
Existing molecular theory $> 10^{-3}\,Jm^{-2}$

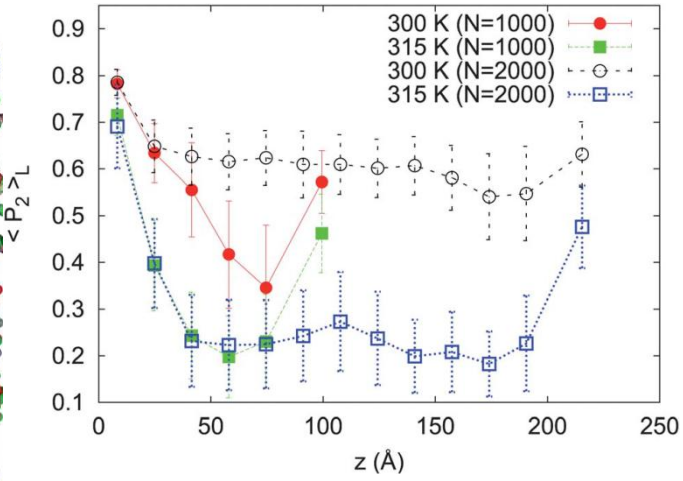
Experiment

$10^{-6} - 10^{-3}\,Jm^{-2}$ **planar**

$10^{-7} - 10^{-5}\,Jm^{-2}$ **homeotropic**

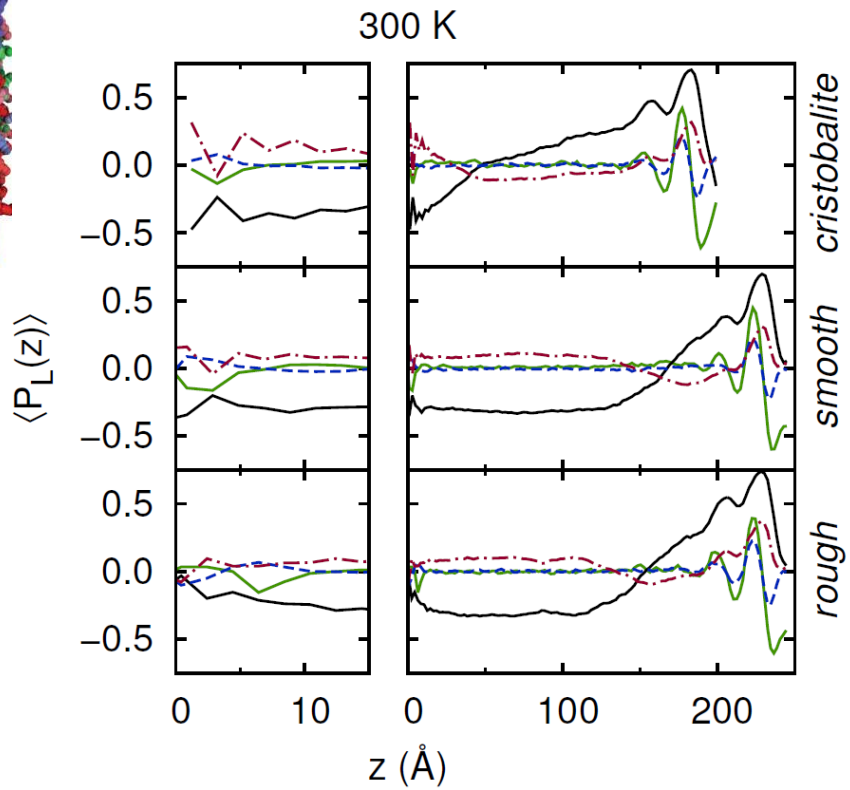
Results of atomistic simulations from Zannoni group

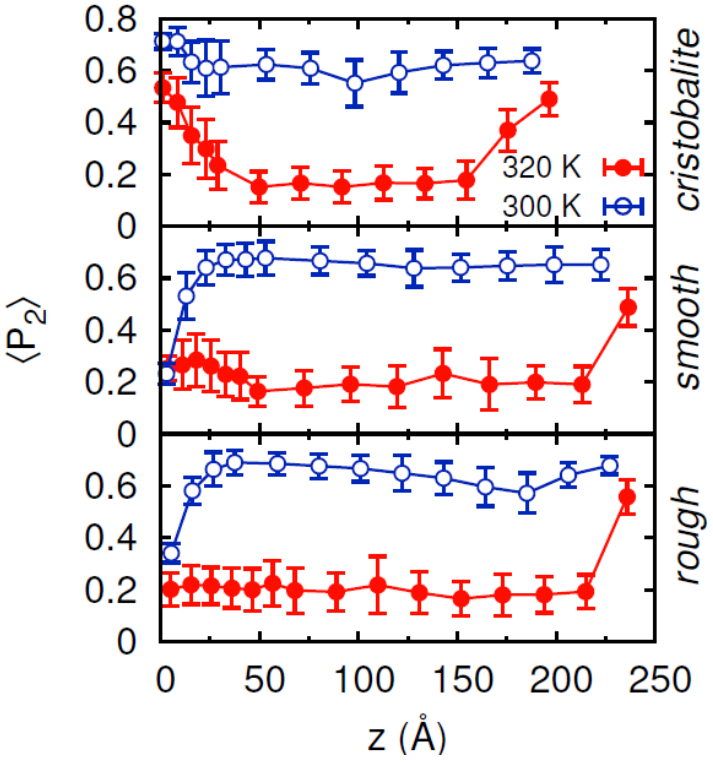




Pizzirusso, A.; Berardi, R.; Muccioli, L.; Ricci, M.; Zannoni, C. Chem. Sci. **2012**, 3, 573

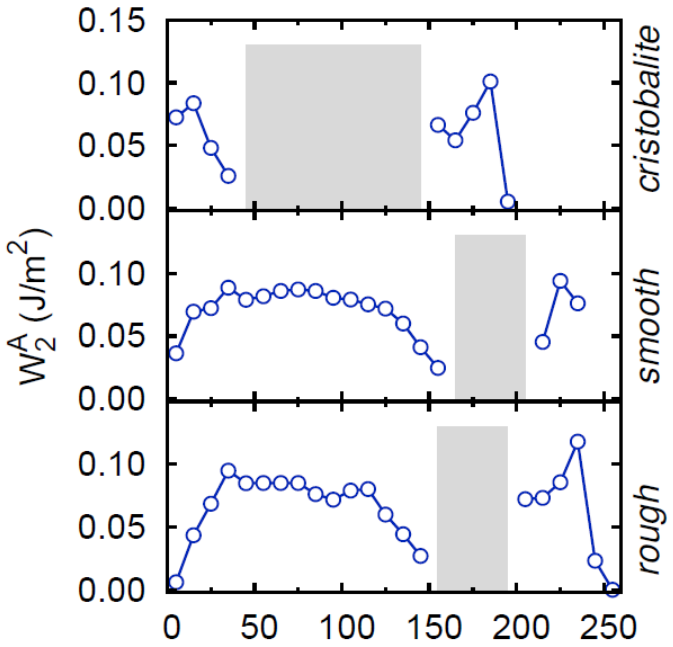
O.M. Roscioni, L.Muccioli, R.G. Della Valle, A. Pizzirusso, M. Ricci, and C. Zannoni. Langmuir, 2013





"What really is anchoring energy ?"

C. Zannoni



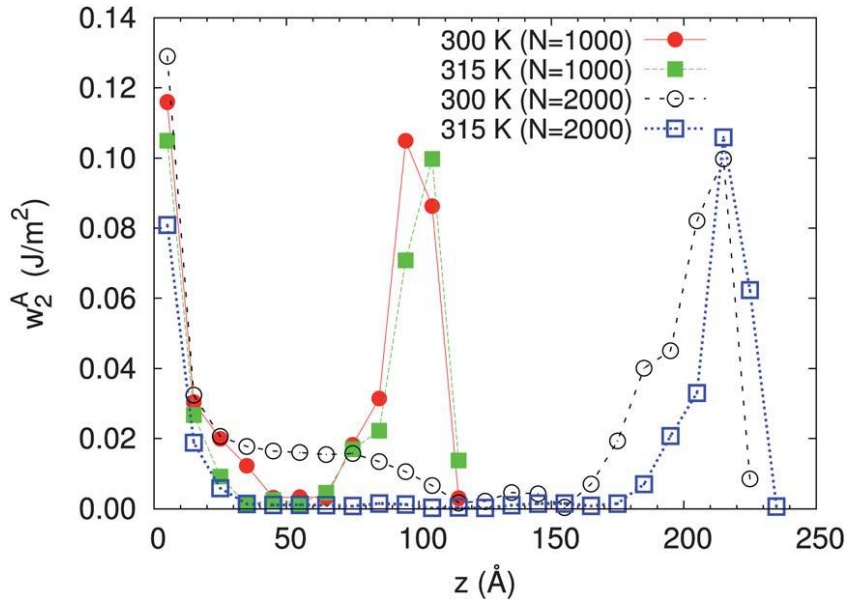
$$W(z) \propto \log \; P(z, \cos\theta)$$

$$P(z,\theta) \propto f_1(z,\omega) \propto \exp(C_1(z,\omega));$$

$$C_1 = C_{10} + \int \rho_0 C_2(z,...)\delta f(\theta) d(2) + ...$$

$$C_2(1,2) = \delta C_1(1)/\delta\rho(2);$$

$$\delta f(\theta) \approx a\theta^2$$

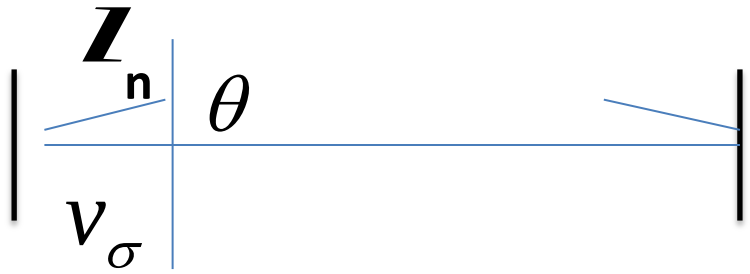


anisotropic direct correlation function tail

$$C_2(z,\theta,....)$$

Possible definition of the anchoring energy

$$W_s = F_\sigma(\theta)$$



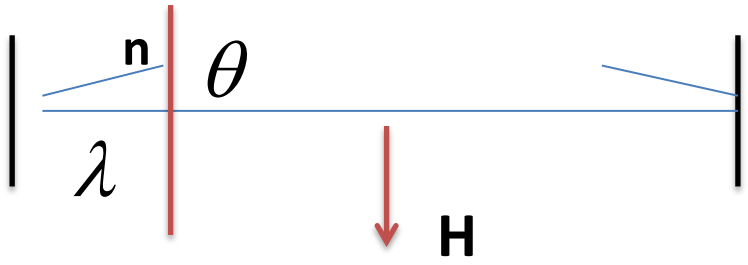
Gibbs potential defined at fixed angle

Neglecting the biaxiality

$$F_\sigma(\theta) \approx F\{n(z)\}$$ **Nonlocal**

$$n_z(0) = 1; \;\; n_z(l) = \cos\theta$$

Simple Frederiksz geometry



Strong anchoring

$$F_d = \int [\frac{1}{2} K(\phi')^2 + H^2 \chi_a \phi^2] dz;$$

$$\phi(-d/2) = 0;\ \phi(d/2) = 0 \Rightarrow\ \theta = \theta_0 \cos qz;\ q^2 = h_c{}^2 = H_c{}^2 \chi_a / K$$

Effective Anchoring energy

$$W(\theta) = \int [\frac{1}{2} K(\phi')^2 + H^2 \chi_a \phi^2] dz;\quad \phi(0) = 0;\ \phi(\lambda) = \theta$$

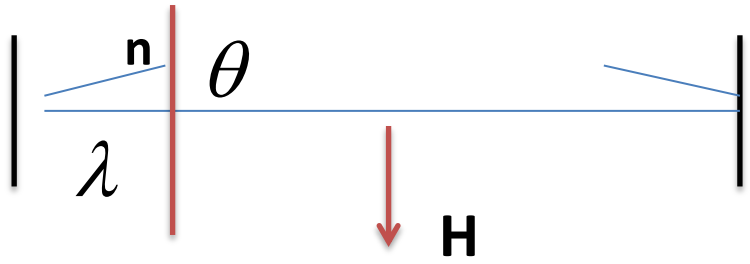
$$\phi = \frac{\theta}{\sin q\lambda} \sin qz;\ q\lambda << 1$$

$$\int_0^\lambda \frac{1}{2} K(\phi')^2 dz \approx \frac{1}{2} K/\lambda;\quad \int_0^\lambda H^2 \chi_a \phi^2 dz \approx (K/2\lambda)(q\lambda)^2 << K/2\lambda$$

$$W_{eff} = K/\lambda$$

Simple Frederiksz geometry

Anchoring energy



$$W(\theta) = \int [K\{n(z)\} + C(z)\phi^2 - h_c{}^2\phi^2]dz \propto W\theta^2$$

$$\phi(\lambda) = \theta; \;\; C(z) = C_0 \exp(-z/l);$$ - correlation tail

$$C_0 >> h^2; \;\Rightarrow\; C_0 \exp(-\lambda/l) \approx h_c^2$$

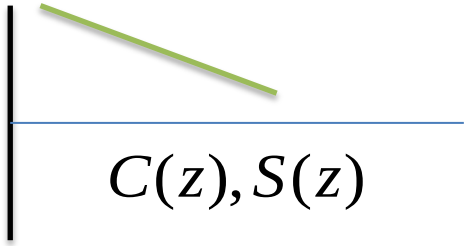
$$W = K/\lambda; \;\; \lambda >> L$$

Some conclusions

Molecular scale

Very strong anchoring of 1-2 molecular layers

Intermediate scale



Correlation tail,
Nonlocal free energy-?
Nonlinear elasticity-?

Macroscopic scale

$$W_s = F_\sigma(\theta) \approx W_0\theta^2$$