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Conference: From DNA-Inspired Physics to Physics-Inspired Biology

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How does helical structure influence correlation forces between DNA?

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How does helical structure influence correlation forces between DNA?

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1.) The counterion-salt-macroion system: a statistical mechanical model

2.) Crude schematic outline of how we calculate the force. Correlation coupling strength.

3.) Direct electrostatic Interaction: Kornyshev-Leikin Theory.

4.) The correlation force: a general expression for weak to intermediate correlation coupling strengths.

5.)The physics of helical dependent correlation forces.

6.) A numerical calculation for univalent ions. Divalent ions?

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Statistical Mechanical Model
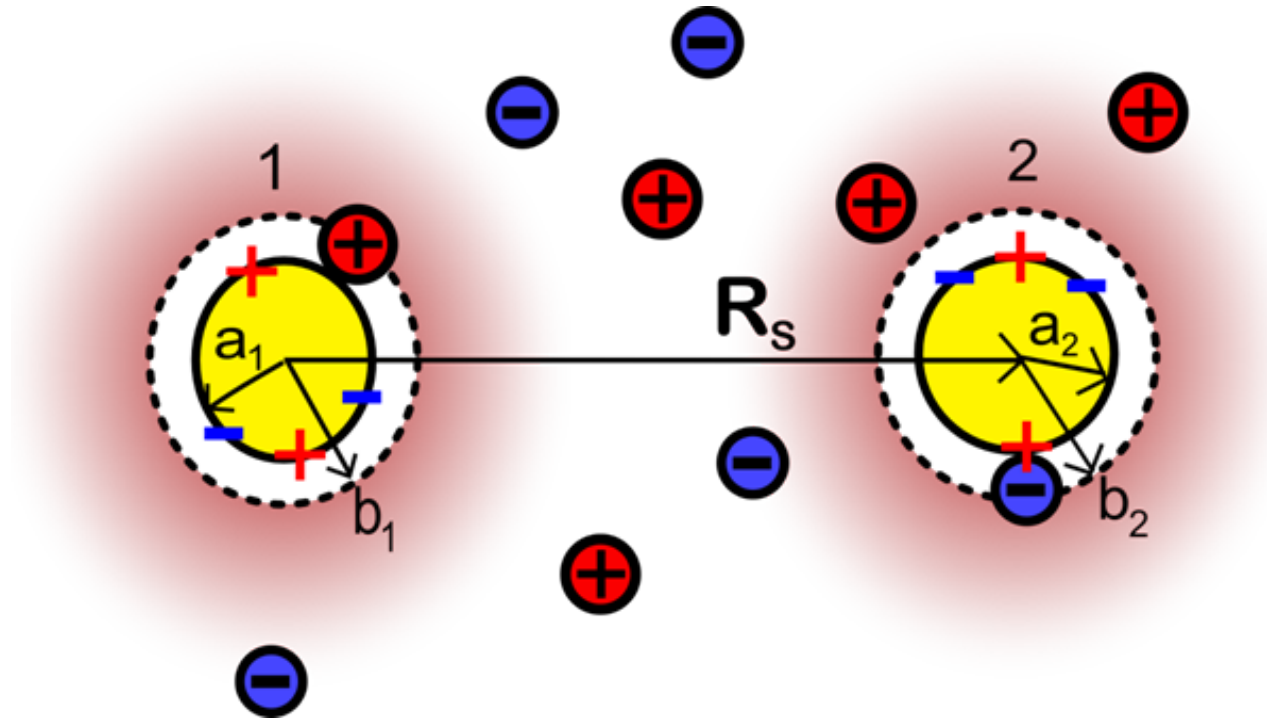
a_1, a_2 -radii of molecular cores where $\varepsilon_c \approx 2$

b_1, b_2 -closest approach radii of ions $b_n = a_n + r_{ion}$, r_{ion} radius of ion.

Solvent with a bulk dielectric $\varepsilon_w \gg \varepsilon_c$

Charge distribution on surface of macro-ion core.

We may write a partition function:

$$Z = \prod_{j=1}^{N} \int d^3 r_j \theta(r_j - b_1) \theta(r_j - b_2) \exp\left(-\beta(E_{\text{int}} + E_{\text{self}})\right) \qquad \beta = 1/k_B T$$

E_{int} is interaction energy (sum of the pair potentials):

$$E_{\text{int}} = \frac{e^2}{2}\left[\sum_{i \neq j} q_i q_j V(\mathbf{r}_i, \mathbf{r}_j) + \int d^3 r \sum_j q_i V(\mathbf{r}_i, \mathbf{r}) \sigma_s(\mathbf{r}) + \int d^3 r \int d^3 r' \sum_j \sigma_s(\mathbf{r}') V(\mathbf{r}', \mathbf{r}) \sigma_s(\mathbf{r})\right]$$

$\sigma_{surf}(\mathbf{r})$ -Surface charge density q_i- valence of ion.

Assume we have only two species one with valance q the other with $-q$

As have interface we need to consider new term:

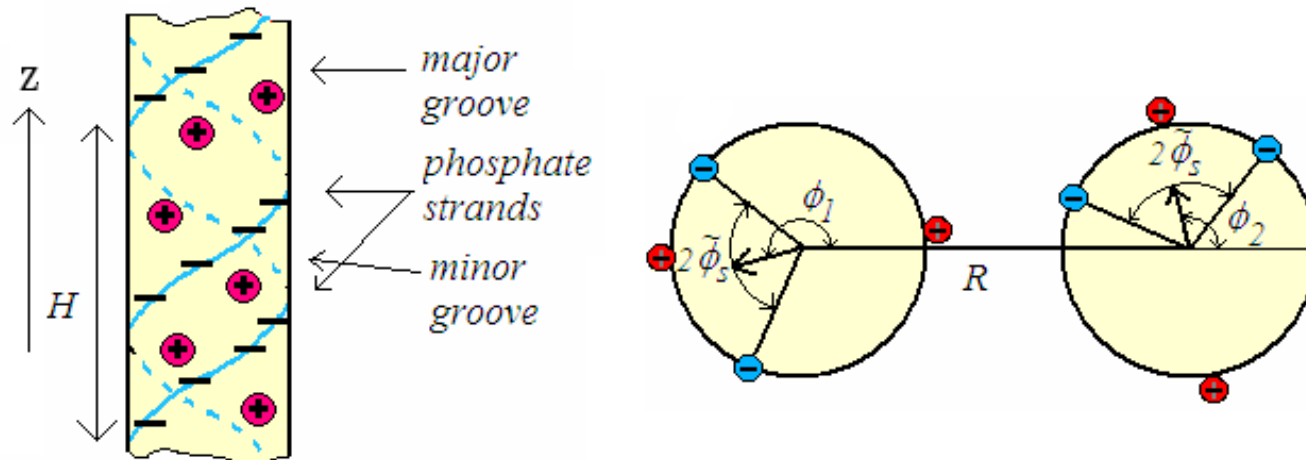$$E_{\text{int}} = e^2 \sum_j q_j^2 \left(V(\mathbf{r}_j, \mathbf{r}_j) - V(\infty, \infty)\right)$$

Also $V(\mathbf{r}_j, \mathbf{r}_j)$ is no longer a simple $1/r$ coulomb form. Must satisfy

$$\chi(\mathbf{r}) \chi(\mathbf{r} - \mathbf{R}_s) \nabla^2 V(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \qquad \chi(\mathbf{r}) = \varepsilon_w \theta(R - a) + \varepsilon_c \theta(a - R)$$

Model for DNA

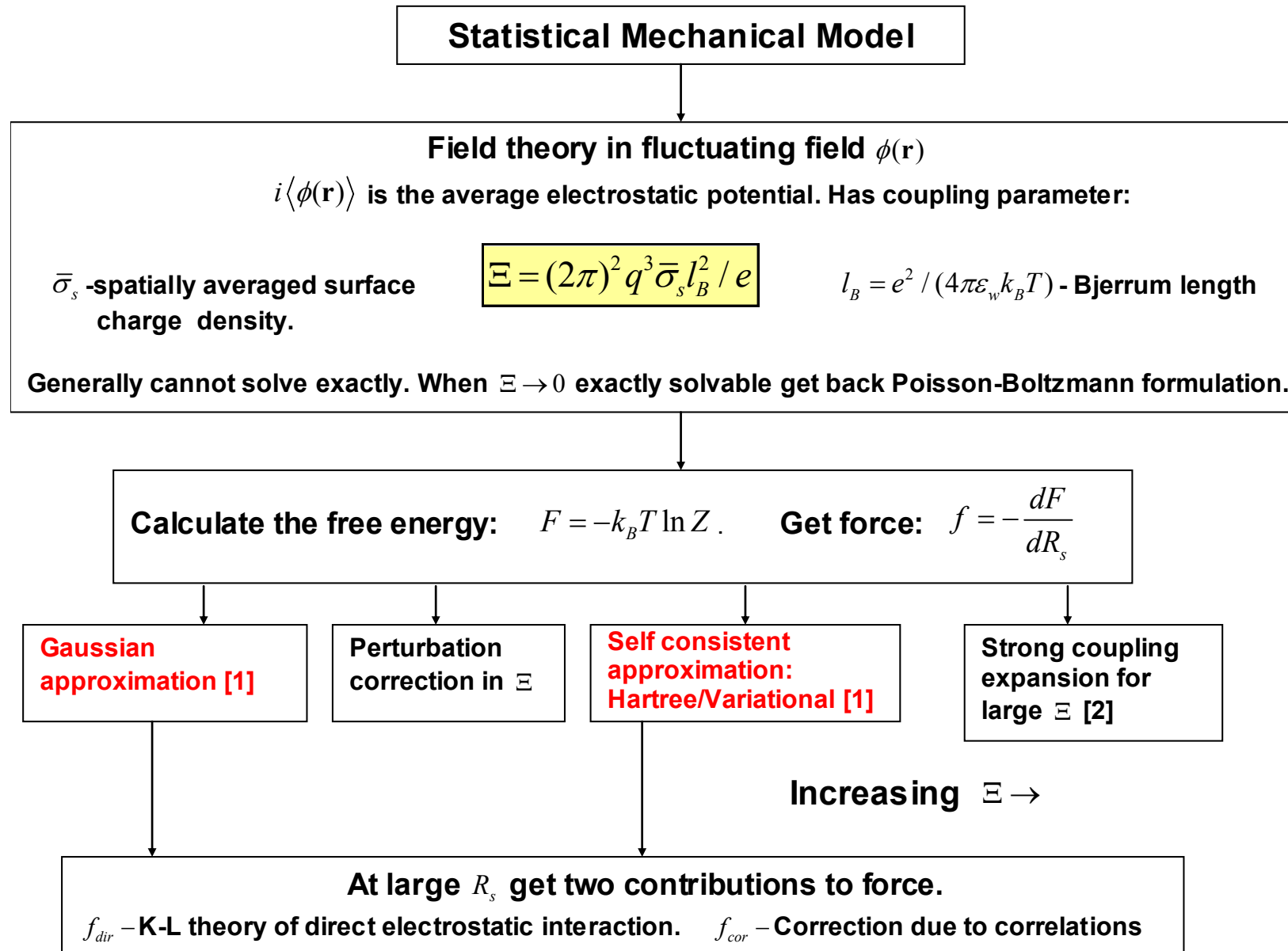Consider parallel DNA molecules of length L. Consider as ideal helices.

Suppose that fraction θ_0 counterions are adsorbed in the grooves of the molecule that contributes to the surface charge distribution.

1.) In centre of minor groove at fraction $f_1\theta_0$ of total phosphate charge..

2.) In centre of major groove at fraction $f_2\theta_0$ of total phosphate charge.

For two DNA molcs: $a_1 = a_2 = a$

Schematic outline of calculation

Statistical Mechanical Model

Field theory in fluctuating field $\phi(\mathbf{r})$

$i\langle\phi(\mathbf{r})\rangle$ **is the average electrostatic potential. Has coupling parameter:**

$\overline{\sigma}_s$ **-spatially averaged surface charge density.**

$$\Xi = (2\pi)^2 q^3 \overline{\sigma}_s l_B^2 / e$$

$l_B = e^2 / (4\pi\varepsilon_w k_B T)$ **- Bjerrum length**

Generally cannot solve exactly. When $\Xi \to 0$ **exactly solvable get back Poisson-Boltzmann formulation.**

Calculate the free energy: $F = -k_B T \ln Z$. **Get force:** $f = -\dfrac{dF}{dR_s}$

Gaussian approximation [1]

Perturbation correction in Ξ

Self consistent approximation: Hartree/Variational [1]

Strong coupling expansion for large Ξ **[2]**

Increasing $\Xi \to$

At large R_s **get two contributions to force.**

f_{dir} **– K-L theory of direct electrostatic interaction.** f_{cor} **– Correction due to correlations**
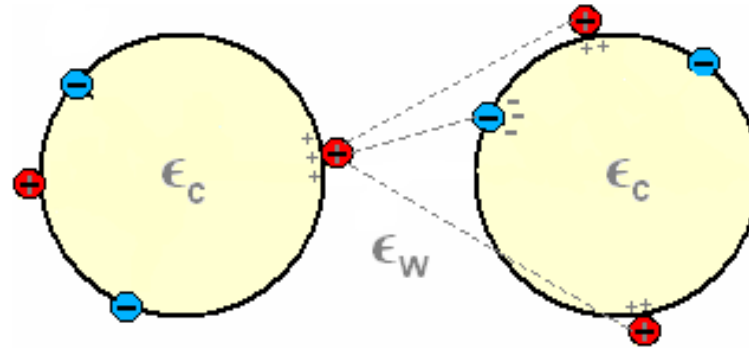
For details: just ask!

Also:[1] D. J. Lee, J. Eur. Phys. E , 2009, 10.1140/epje/i2008-10436-x
[2] M. Kanduc, J. Dobnikar, R. Podgornik, Soft Matt., 2008, **5**, 868

K-L Theory for direct electrostatic interaction

$$f_{dir} = -\frac{dE_{dir}}{dR_s}$$

$$E_{dir} = L\sum_n (-1)^n A_n(R_s)\cos(-n(\phi_1 - \phi_2))$$

At large R (neglect image charge repulsion) have for direct electrostatic interaction.

$$A_n(R_s) \approx \frac{\bar{A}_n}{\sqrt{\kappa_n R}}\exp(-\kappa_n R_s)$$ where $\kappa_n = \sqrt{\kappa_D^2 + n^2 g^2}$ and $g = 2\pi / H$

Correlation terms

$$f_{Corr} = -\frac{dE_{Corr}(R_s)}{dR_s}$$

$$E_{Corr}(R_s) = -L\Xi\sum_{n}(-1)^n B_n(R_s)\cos(n(\phi_1-\phi_2))$$

$$B_n(R_s) \approx \bar{B}_n(R_s)\exp(-\hat{\kappa}(ng)R_s)$$

$$\hat{\kappa}(ng) = \sqrt{4\kappa_D + n^2 g^2}$$ -Decay faster than direct interaction terms.

$\bar{B}_n(R)$ is a slowly varying function with respect to R compared with exponential.

Depends on the 'helical' Fourier components of excess number density $n_{ex}(n,r)$
- amount the number density of small ions exceeds c_{salt} , bulk salt concentration

If $n_{ex}(n,r) = \tilde{n}_{ex}(n)\delta(r-b)$, confined to a thin layer then $B_n(R_s) \propto (b\tilde{n}_{ex}(n))^2$

In Gaussian approximation : $n_{ex}(n,r) = c_{salt}\int_0^{2\pi} d\tilde{\phi}\left(\cosh\psi(r,\tilde{\phi})-1\right)\exp(-in\tilde{\phi})$ $\tilde{\phi} = \phi - gz$

(similar expression for Hartree approx)

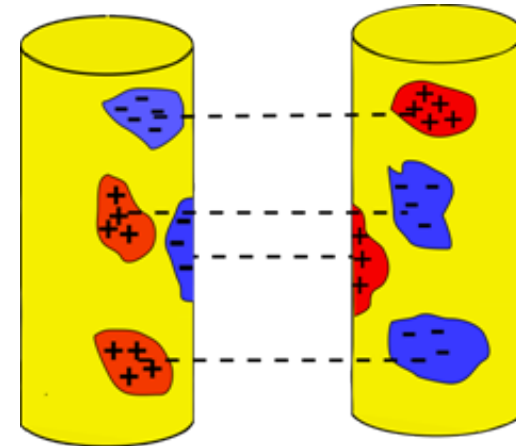$\psi(r,\tilde{\phi})$ - reduced potential calculated for a single DNA molecule using PB equation.

At large separations can neglect adjustment of ions due to field of other molecule

Can include a contribution from groove bound ions. Free to adjust to fluctautions or not?

In general (neglecting image charges):

$$B_n(R_s) \propto \int_{-\infty}^{\infty} dq\, T(n,q,R_s)^2 \exp\left(\frac{R_s}{2}(\hat{\kappa}(2q-ng)+\hat{\kappa}(2q+ng)-2\hat{\kappa}(ng))\right)$$

$$T(n,q,R_s) = \frac{1}{a}\int_{a}^{R_s/2} rdr\, I\left(\frac{r}{2}(\hat{\kappa}(2q-ng)+\hat{\kappa}(2q+ng)-2\hat{\kappa}(ng))\right)n_{ex}(n,r)$$

For uniformly charged cylinders only have $-B_0(R_s)$ a purely attractive interaction.

Comes from correlations between fluctuations in charge density of small ions.

Fluctuations of net positive charge on one molc. induce fluctuations of negative charge on the other molecule. Visa-versa.

The size of the fluctuations depend the number density of ions- both negative and positive ions can be displaced to create a charge fluctuation.

The strength of interaction depends on the product of the size of fluctuation on both molecules

Number density
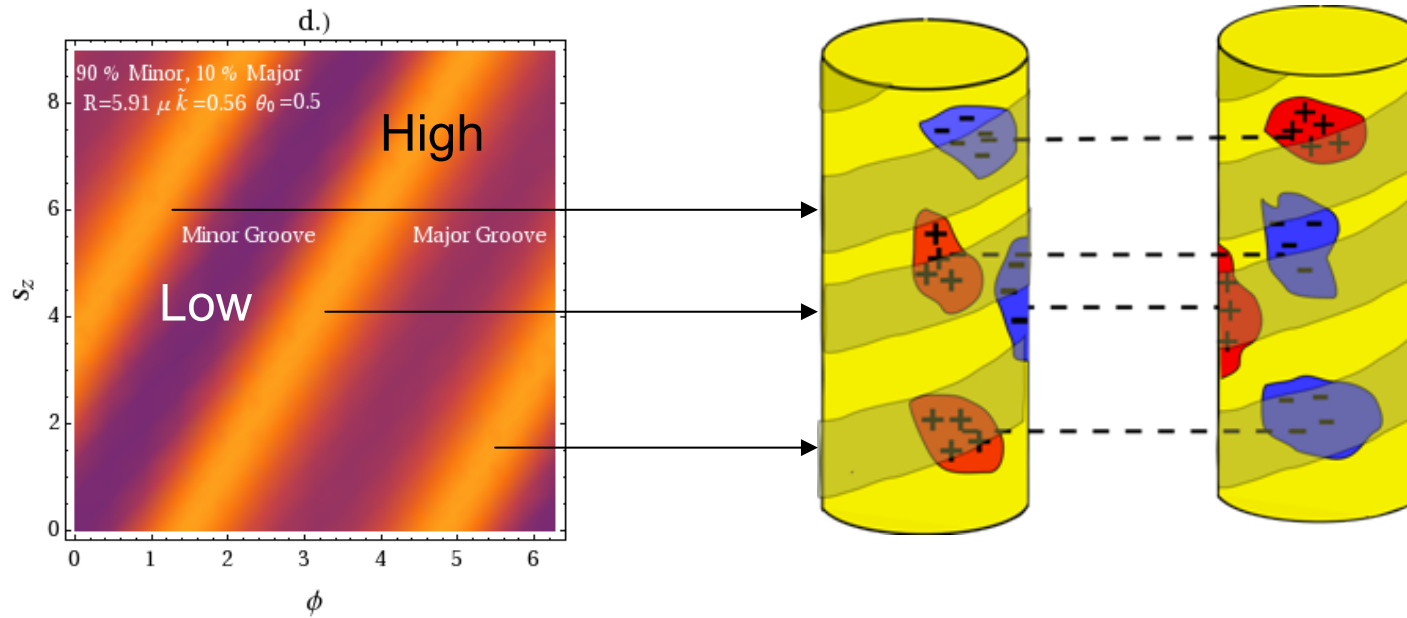
If the surface charge density on the molecule is not uniform: helical charges modulate small ion number density.

The helical structure modulates the size of the fluctuations through number density $\rightarrow B_1(R_s), -B_2(R_s)$.

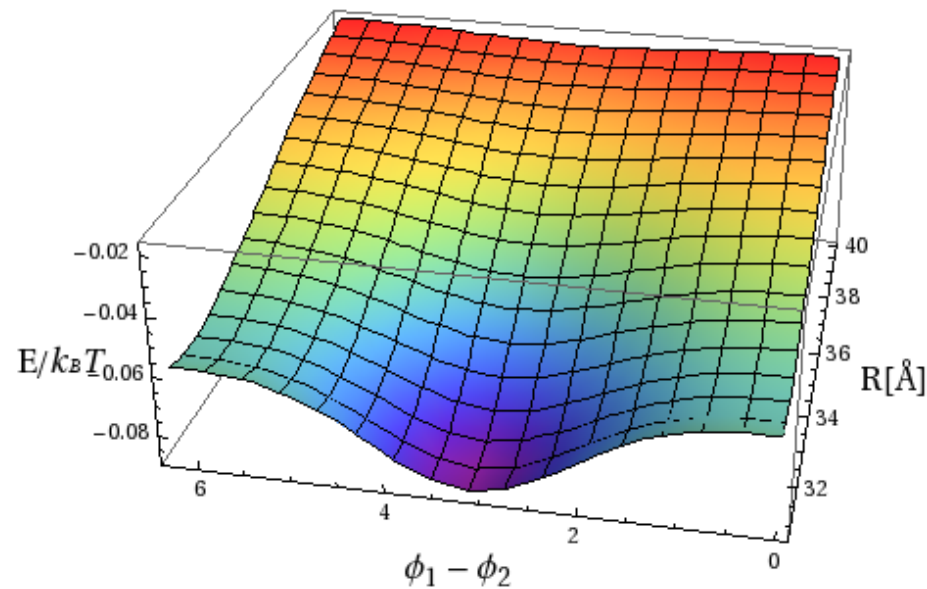Signs all opposite to direct interaction.

Electrostatic zipper:

Maxima in charge density (positive regions) on molc. want align with minima (negative regions) on other molc.

Correlation zipper:

Maxima in number density on one molc. want to align with maxima in number density on other molc.

Numerical Result for E$_{Corr}$

q=1 (univalent) $f_1 = f_2 = 0.5$, $\theta = 0.4$, $L = 500\text{Å}$. Groove adsorbed ions fixed.

Calculated for Gaussian approximation. Correlation energy very small for $q = 1$

For divalent ions E_{corr} could be much more than this and so significant.

$\Xi \sim q^3$ also expect helical components of number density to be much larger.

Implications

When correlation forces are important (low solvent dielectric, multivalent ions):

1.) New optimum azimuthal orientations. For correlation forces alone: when $B_1(R_s) > B_2(R_s)$ (large R_s) $\phi_1 - \phi_2 = \pi$ and when $B_1(R_s) < B_2(R_s)$ (small R_s) $\phi_1 - \phi_2 = 0$ discontinuous jump between the two minima. Different frustrated states in assemblies, transitions more abrupt. Frustration at interaxial large separations not small separations.

2.) Correlation forces may favour cholesteric pitch of opposite sign to direct electrostatic terms.

3.) Correlation forces get more enhanced by undulations than direct electrostatic terms as have shorter decay lengths.

Correlation forces probably most important for small multivalent ions that do not bind well to DNA. Hope soon to do some work on divalent ions.