Solvation, Structural and Hydration Forces

Chapter 13
Non-DLVO Forces

• When two surfaces or particles approach closer than a few nanometres, continuum theories of van der Waals and double-layer forces often fail to describe their interaction.
• This is either because one or both of these continuum theories breaks down at small separations or because other non-DLVO forces come into play.
• Solvation forces depend not only on the properties of the intervening medium but also on the chemical and physical properties of the surfaces.
Molecular Ordering at Surfaces, Interfaces and in Thin Films

• The short-distance intermolecular pair potential can be quite different from that expected from continuum theories.
• The short-distance interactions are usually referred to as solvation forces, structural forces, or – when the medium is water – hydration forces.
• The solvation (or structuring) of solvent molecules at a surface is determined primarily by the geometry of molecules and how they can pack around a constraining boundary.
Density profile
Origin of Main type of Solvation Force: The Oscillatory Force

- The repulsive double-layer pressure between two charged surfaces separated by a solvent containing the surface counterions is given by the contact value theorem.
  \[ P(D) = kT \left[ \rho_s(D) - \rho_s(\infty) \right] \]  \hspace{1cm} (13.4)
- This equation also applies to solvation forces so long as there is no interaction between the walls and liquid molecules.
- A solvation force arises once there is a change in the liquid density at the surfaces as they approach each other.
How the molecular ordering changes as the separation $D$ changes

![Diagram of molecular ordering changes with varying $D$](image)

![Graph showing pressure changes with varying $D$](image)
Origin of Main type of Solvation Force: The Oscillatory Force

• It is important to note that it is more correct to think of the solvation force as the van der Waals force at small separations with the molecular properties and density variations of the medium taken into account.

• It is also important to appreciate that solvation forces do not arise simply because liquid molecules tend to structure into semi-ordered layers at surfaces. They arise because of the disruption or change of this ordering during the approach of a second surface. If there were no change, there would be no solvation force.
Measurements and Properties of Solvation Forces: Oscillatory forces in Non-Aqueous Liquids.

- While theoretical work relevant to practical systems is still in its infancy, there is a rapidly growing literature on experimental measurements and other phenomena associated with solvation forces.
- The oscillations can be smeared out if the molecules are irregularly shaped, e.g., branched, and therefore unable to pack into ordered layers.
Measurements and Properties of Solvation Forces: Oscillatory forces in Non-Aqueous Liquids.

• (1) *Inert, spherical, rigid molecules*: In liquids such as CCl₄, benzene, toluene, and cyclohexane whose molecules are roughly spherical and fairly rigid ⇒ the periodicity of the oscillatory force is equal to the mean molecular diameter $\sigma$.

• (2) *Range of oscillatory forces*: The peak-to-peak amplitudes of the oscillations show a roughly exponential decay with distance with a characteristic decay length of 1.2 to 1.7 $\sigma$. 
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• (3) **Magnitude of forces**: The oscillatory force can exceed the van der Waals force at separations below five to 10 molecular diameters, and for simple (non-polymeric) liquids, merges with the continuum van der Waals or DLVO force at larger separations.

• (4) **Effect on adhesion energy**: The depth of the potential well at contact (D=0) corresponds to an interaction energy that is often surprisingly close to the value expected from the continuum Lifshitz theory of van der Waals forces (Section 11.10).
Measurements and Properties of Solvation Forces: Oscillatory forces in Non-Aqueous Liquids.

- (5) **Effects of water and other immiscible polar components**: The presence of even trace amounts of water can have a dramatic effect on the solvation force between two hydrophilic surfaces across a non-polar liquids. This is because of the preferential adsorption of water onto such surfaces that disrupts the molecular ordering in the first few layers. (Section 15.6)

- (6) **Small flexible (soft) molecules**: Their short-range structure and oscillatory solvation force does not extend beyond two to four molecules.
Measurements and Properties of Solvation Forces: Oscillatory forces in Non-Aqueous Liquids.

• (7) *Linear chain molecules*: Homologous liquids such as n-octane, n-tetradecane and n-hexadecane exhibit similar oscillatory solvation force laws. For such liquids, the period of the oscillations is about 0.4nm.

• (8) *Non–linear (asymmetric) and branched chain molecules*: The liquid film remains disordered or amorphous and the force law is not oscillatory but monotonic.
Measured force laws between mica surfaces
Measurements and Properties of Solvation Forces: Oscillatory forces in Non-Aqueous Liquids.

- (9) **Effect of molecular polarity (dipole moment and H-bonds)**: The measured oscillatory solvation force laws for polar liquids are not very different from those of non-polar liquids of similar molecular size and shape.

- (10) **Effect of surface structure and roughness**: The structure of the confining surfaces is just as important as the nature of the liquid for determining the solvation forces. As we have seen, between two surfaces that are completely smooth (or unstructured) the liquid molecules will be induced to order into layers, but there will be no lateral ordering within the layers. In other words, there will be positional ordering normal but not parallel to the surfaces.
Measurements and Properties of Solvation Forces: Oscillatory forces in Non-Aqueous Liquids.

- However, if the surfaces have a crystalline (periodic) lattice, this will induce ordering parallel to the surfaces as well, and the oscillatory force will now also depend on the structure of the surface lattices.

- On the other hand, for surfaces that are randomly rough, the oscillatory force becomes smoothed out and disappears altogether, to be replaced by a purely monotonic solvation force.
Solvation of Forces in Aqueous Systems: Repulsive ‘Hydration’ Forces

• There are many other aqueous systems where DLVO theory fails and where there is an additional short-range force that is not oscillatory but smoothly varying, i.e., monotonic. → exponentially repulsive b/n hydrophilic surfaces: repulsive hydration or structural force
  (whenever water molecules strongly bind to surfaces containing hydrophilic groups or H-bonding groups)

■ Strength: E needed to disrupt the H-bonding network and/or dehydrate two surfaces
Two types of Repulsive ‘Hydration’ Forces (1)

- Steric hydration forces b/n fluid-like amphiphilic surfaces
  - Measured across soap films composed of various surfactant monolayers as well as across uncharged bilayers composed of lipids with zwitterionic or sugar headgroups
  - Force range: 1-2 nm, Exponential decay length: 0.1-0.3 nm; both increase with the temp. and ‘fluidity’ of highly mobile amphiphilic structures
  - Origin of this force: entropic-arising from overlap of thermally excited chains and headgroups protruding from these surfaces (CH 14 & 18)
Two types of Repulsive ‘Hydration’ Forces (2)

• Repulsive hydration forces b/n solid crystalline hydrophilic surfaces
  ✓ In the case of silica, mica, certain clays and many hydrophilic colloidal particles
  ✓ Arising from strongly H-bonding surface group (hydrated ions or –OH)
    → Relatively long-range force (Force range: 3-5nm, decay length: 1nm)
  ✓ Empirical relation of the hydration repulsion

\[
W = + W_0 e^{-D/\lambda_0}
\]

\(\lambda_0 \approx 0.6-1.1 \text{ nm for 1:1 electrolytes}
\)

\(W_0 < 3-30 \text{ mJ/m}^{-2}\)

Between two silica surfaces in various aqueous NaCl solutions
Two types of Repulsive ‘Hydration’ Forces (2)

In dilute electrolyte solutions (<10^{-4}) : DLVO theory

- At higher salt conc. (>10^{-3}) hydrated cations bind to the negatively charged surfaces and give rise to a repulsive hydration force
  - the strength and range of the hydration forces increase with the hydration number of cations: Mg^{2+} > Ca^{2+} > Li^{+} ~ Na^{+} > K^{+} > Cs^{+}

  c.f.) acid solution: only proton ions

- Measured forces b/n curved mica surfaces in KNO₃ or KCl solutions
  - Force range: 3-4 nm, Exponential decay length: 1 nm, Short-range oscillations of periodicity 0.22-0.26 nm
Two types of Repulsive ‘Hydration’ Forces (2)

- Exhibiting oscillations of mean periodicity of $0.25 \pm 0.03$ nm, roughly equal to the diameter of the water molecule, below about 1.5 nm
- The first three minima at $D \approx 0, 0.28$ and 0.56 nm at negative energies
- Clay plates such as motomorillonite: repelling each other increasingly strongly down to separations of $\sim 2$ nm vs. stacking into stable aggregates with water interlayers of 0.25 and 0.55 nm thickness
Two types of Repulsive ‘Hydration’ Forces (2)

• Hydration forces can be modified or regulated by exchanging ions of different hydrations on surfaces
  ✓ Hydration regulation in colloidal dispersions: the effects of different electrolytes on the hydration forces between colloidal particles can determine whether they will coagulate or not

Domains of stability and instability of amphoteric PS latex particles, composed of –COO\(^-\) and –NH\(_3\)\(^+\) groups in (a) CsNO\(_3\) and (b) KNO\(_3\)

(b) is more stable due to the stronger hydration of K\(^+\) than Cs\(^+\)
Two types of Repulsive ‘Hydration’ Forces (2)

- The effectiveness of cation as coagulants decreases according to ‘lyotropic series’
  \[ \text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+, \quad \text{Ca}^{2+} > \text{Mg}^{2+} \]
  ✓ Computer simulation of interaction b/n alkali metal and chloride ions
    depth of the primary potential minimum : \( \text{Li}^+\text{Cl}^- > \text{Na}^+\text{Cl}^- > \text{K}^+\text{Cl}^- \)
  ✓ The repulsion in water : \( \text{K}^+ - \text{K}^+ > \text{Na}^+ - \text{Na}^+ > \text{Li}^+ - \text{Li}^+ \)

- Repulsive hydration forces can be used as follows
  ✓ Unexpectedly thick wetting films of water on silica (ch 12.9)
  ✓ Clay swelling, ceramic processing and rheology, and colloidal and bubble coalescence
The intrinsic nature of hydration force

• The hydration force is not of a simple nature
  ✓ It is probably the most important yet the least understood of all the forces in liquids
  ✓ The nature of the surfaces is equally important: ion exchange (adding more salt or changing the pH for hydrophobic surface, chemical modifying for hydrophilic surface)

• How do exponentially decaying hydration forces arise?
  ✓ A monotonic exponential repulsion or attraction, possibly superimposed on an oscillatory profile; simply additive with the monotonic hydration and DLVO forces with different mechanisms.
  ✓ The short-range hydration force b/n all smooth, rigid or crystalline surfaces has an oscillatory components.
Solvation of Forces in Aqueous Systems: 

**Attractive ‘Hydrophobic’ Forces**

- A hydrophobic surface cannot bind to water molecules via ionic or hydrogen bonds; entropically unfavorable !!
  \[\rightarrow \text{attractive force b/n hydrophobic surfaces (hydrocarbon and fluorocarbons)}\]

- Accumulated experimental data of this force
  - Mica surfaces coated with surfactant monolayers exposing hydrocarbon or fluorocarbon groups
  - Silica and mica surfaces with rendered hydrophobic by chemical methylation or plasma etching

  \[\rightarrow \text{the hydrophobic force law b/n two macroscopic surfaces is of surprisingly long range, decaying exponentially with a decay length of 1-2 nm in the range 0-10nm, hydrophobic force >> van der Waals attraction}\]
Examples of attractive hydrophobic interactions in aqueous solutions

(a) Low solubility/immiscibility (CH15, 16)
(b) Micellization (CH 16)
(c) Dimerization and association of hydrocarbon chains
(d) Protein folding
(e) Strong adhesion
(f) Non-wetting of water on hydrophobic surfaces
(g) Rapid coagulation of hydrophobic or surfactant-coated surfaces
(h) Hydrophobic particle attachment to rising air bubbles
Solvation of Forces in Aqueous Systems:

**Attractive ‘Hydrophobic’ Forces**

- Attractive hydrophobic forces [AHF] can be judged from measurements of their interfacial energy with water $\gamma_i$ or from the contact angle of water on them (CH 15)

\[
W = -2\gamma_i e^{-D/\lambda_0}
\]

in the range 0-10 nm, $\gamma_i = 10-50$ mJm$^{-2}$, $\lambda_0 = 1-2$ nm

- $D < 10\text{nm}$, AHF is insensitive or only weakly sensitive to electrolyte ions and their conc.

$D > 10\text{nm}$, AHF does depend on the intervening electrolyte, and that in dilute solutions, or solutions containing divalent ions, it can continue to exceed the vdwS attraction out to separation of 80nm.
Solvation of Forces in Aqueous Systems: **Attractive ‘Hydrophobic’ Forces**

- The origin of the hydrophobic force is still unknown.
- Monte Carlo simulation of the interaction between two hydrophobic surfaces across 1.5nm water → Decaying oscillatory force!
- Hydrocarbon/ethylene-oxide interface
  - From being strongly hydrophilic (top curve) to strongly hydrophobic (bottom curve)
  - Increasingly more hydrophobic at higher temp.
  - The hydration force can be far stronger than any of the DLVO forces.

Example of increasing attraction with temperature characteristic of hydrophobic forces
Chapter 14.

Steric and Fluctuation Forces
Diffuse Interface

Diffuse surface = Dynamically rough (thermally mobile surface groups)

Inherently mobile or fluid-like Surface

Chain molecules attached to a surface, dangled out into the solution → polymer covered surface
What is a Polymer?

Polymer:
Macromolecule composed of many monomers

Copolymer: ~A-B-A-B~
Volume of Polymers

Unperturbed Random Coil

- **Unperturbed radius of gyration,** $R_g$

$$R_g = \frac{l\sqrt{n}}{\sqrt{6}} = \frac{l\sqrt{M/M_0}}{\sqrt{6}}.$$ 

$n = \# \text{ of segments}$

$l = \text{effective segment length,}$

(Only in ideal solvent!)

- **Flory radius,** $R_F = \alpha R_g \approx ln^{3/5}$ (in real solvents)

($\alpha$: Intermolecular expansion factor)

Good solvent: repulsion btw. segments ($\alpha < 1$)

Poor solvent: attraction btw. segments ($\alpha > 1$)

Theta temperature, $T_\theta$: ideal solvent ($\alpha = 1$)
Polymers at Surfaces

In solution  Chemisorbed  Physisorbed

Low coverage  high coverage  Bridging
Repulsive Steric Forces between Polymer-Coated Surfaces

Force development process

Factors affecting steric force

- Coverage of polymer on each surface
- Reversible adsorption or irreversible grafting onto the surface
- Quality of the solvent

Outer segments overlap
⇒ Repulsive steric force
Consider repulsive steric interaction between surfaces containing an adsorbed polymer layer where each molecule is grafted at one end to the surface but is otherwise inert.

1) At low surface coverage

- No overlap of neighboring chains
- Each chain interact with the opposite surface independent of other chains

Repulsive energy per unit area for two surfaces in a theta solvent over the distance from $D=8R_g$ down to $D=2R_g$:

$$W(D) = 2\Gamma kT e^{-D^2/4R_g^2} + ... \approx 36\Gamma kTE^{-D/R_g}$$

$W(D) \approx 36\Gamma kT e^{-D/R_g}$ per molecule

$\Gamma$ : number of grafted chains per unit area
$\Gamma = \frac{1}{s^2}$ (s: mean distance between attachment point)

Valid for low coverage $s > R_g$
when layer thickness (L) is equivalent to $R_g$

Layer thickness
- In theta solvent : vary as $M^{0.5}$
- In good solvent : vary as $M^{0.6}$

$L = R_g = \frac{l\sqrt{n}}{\sqrt{6}} = \frac{l\sqrt{M/M_0}}{\sqrt{6}} \propto M^{1/2}$

$L = R_F = l \cdot n^{3/5} = l \cdot (M/M_0)^{3/5} \propto M^{0.6}$
2) At high surface coverage (Brush)

- Adsorbed or grafted chains close to each other
  ⇒ Chains are forced to extend away from the surface much farther than $R_g$

- Brush Layer thickness
  - End-grafted chain: $L \propto M$
  - General equation for brush in a theta solvent
    \[ L \propto M^\nu \propto n^\nu \quad \nu : 0.5 \sim 1 \text{ (from low to high coverage)} \]
  - For a brush in a good solvent

\[
L = \frac{nl^{5/3}}{s^{2/3}} = \Gamma^{1/2} R_F^{5/3}
\]

\[
\Gamma = \frac{1}{s^2}
\]

$R_F = \ln^{3/5}$
Theories of Steric Interaction III

Alexander-de Gennes theory

- Repulsive pressure between two brush-bearing surfaces closer than 2L

\[
P(D) \approx \frac{kT}{s^3} \left(2L / D\right)^{9/4} - \left(D / 2L\right)^{3/4}
\]

for \( D < 2L \)

- Osmotic repulsion between the coils
  - favor stretching
  - increase \( D \)

- Elastic energy of the chain
  - Oppose stretching
  - Decrease \( D \)

- For \( 0.2 < D/2L < 0.9 \),

\[
P(D) \approx \frac{100kT}{s^3} e^{-\pi D/L} = \frac{100kT}{s} \Gamma e^{-\pi D/L}
\]

\[
W(D) \approx \frac{100L}{\pi s^3} kTe^{-\pi D/L} = \frac{100L}{\pi s} \Gamma kTe^{-\pi D/L}
\]

\( W = Fs \)
Steric forces between surfaces with end-grafted chains

- End-grafted polymers: well understood
  - Each molecule is attached to the surface at one end
  - Coverage is fixed
  - Molecules do not interact either with each other or with the two surfaces
  - Ex) Di-block copolymer
    One block for anchoring, the other protruding into the solvent to form polymer layer

Fig 14.3 Forces between two polystyrene brush layers end-grafted onto mica surfaces in toluene

- Measured forces agree with theoretical fits of Alexander - de Gennes eqn.
- No hysterisis on approach and separation of polymers
Steric forces between surfaces with physisorbed layers I

- No anchoring group that chemisorb to the surface
- Binding to the surface via much weaker physical forces
- Highly dynamic layers
  : Individual segments continually attaching and detaching from the surface
  : Whole molecules slowly exchange with those in bulk solution

When two surfaces approach each other

- Amount of adsorbed polymer changing
- Number of binding sites per molecule changing
- Different segments from the same coil bound to both surfaces ⇒ Bridging
- Long time to reach equilibrium
- Hysteretic force profile
Steric forces between surfaces with physisorbed layers II

Forces between two polyethylene oxide layers physisorbed onto mica
Solvent: aqueous 0.1M potassium nitride
- Hysterisis on approach and separation of physisorbed polymer

Evolution of the forces with the time allowed for high MW polymer to adsorb from solution
- time ↑, adsorption ↑, brush layer ↑
- Gradual reduction in the attractive bridging component

The range of repulsive steric force may be many times \( R_g \) (\( > 10 \ R_g \))
Polymer molecules are surrounded by molecules of its own kind

⇒ Much the same interactions as that of a polymer in a theta solvent

Terminally anchored to the surface

\[
W(D) = 2\Gamma kTe^{-D^2/4R_g^2} + \ldots \approx 36\Gamma kTe^{-D/R_g} \\
W(D) \approx 36kTe^{-D/R_g}
\]
### Experimental force behavior in Pure Polymer Liquid

| Forces between mica surfaces across pure polymer melts | At small distance: Oscillations with a periodicity equal to the segment width
| Non-equilibrium monotonically decaying repulsion farther out up to $10R_g$  
| : Strong binding or effective immobilization of polymers at the surface |

| Forces between inert hydrocarbon surfaces across chain-like hydrocarbon liquids | Attractive tail  
| ⇒ Much weaker binding to the surfaces |

| Forces between irregularly shaped polymers (e.g. bumpy segments or randomly branched side group) | No short range oscillation, but smooth monotonic repulsion  
| ⇒ Inability to order into discrete, well-defined layers |

**Limitation of force measurement** in polymer molecules concentrated within adsorbed surface layer or confined within a thin film between two surfaces:

- Molecular relaxation time higher than in the bulk
- Liquid molecules in the bulk freeze into amorphous glassy state at the surface

⇒ *Measurement not at true thermodynamic equilibrium*
Polymer segments

Segments attract each other in a **poor solvent**: van der Waals force, solvation forces

- Isolated coil shrinks below $R_g$ in solution

Polymer-coated surfaces

- As two **polymer-coated surfaces** come together in poor solvent,
  
  **Attraction between the outermost segments**

  $\Rightarrow$ **Initial Intersegment attraction between surfaces**

- As two polymer-coated surfaces come closer,
  
  **Steric overlap repulsion wins out**
Interactions between grafted and adsorbed polystyrene layers below the theta temperature in poor solvent

(a) End-grafted polystyrene brush in toluene ($\theta = 35 \degree C$)

(b) Physisorbed polystyrene in cyclohexane ($\theta = 34.5 \degree C$)

Attractive Intersegment Forces / Bridging forces

Rg = 7 nm
Rg = 11 nm

Attraction due to intersegment force

21$\degree$ C

Rg = 8.5 nm
Rg = 21 nm

Attraction due to Bridging force

Interactions between grafted and adsorbed polystyrene layers below the theta temperature in poor solvent
# Attractive Bridging Forces

| Requirement                  | Segment – surface force: attractive  
|                             | Available binding sites for segments on the opposite surface |
| Bridge formation            | Polymer coil will form bridge between two surfaces  
|                             | ⇒ Attractive bridging force between two surfaces |
| Dependence on coverage      | Coverage too high (brush), few free binding sites for bridges  
|                             | ⇒ Brush layer thicker than $R_F$, no bridging attraction |
|                             | Coverage too low, density of bridges will be low |
| Dependence on distance      | Bridging force decays exponentially with distance  
|                             | Decay length $\approx R_g$ of the tail and/or loops on the surfaces |
| Strength                    | under suitable conditions, Sometimes strong far exceeding van der Waals interaction |
Effect of surface coverage and solvent quality

By polymer property
(Reactivity, M.W. ...)

Effect of surface coverage and solvent quality on force profiles of adsorbed and grafted chains
Attractive Depletion Forces I

• Polymers repelled from surfaces
  ⇒ no adsorption from solution at all

• Two surfaces in a dilute solution of coils of average radius Rg
  • Polymer coils have no interaction with the surface

  When surfaces are closer than Rg, coils will be pushed out from the gap
  ⇒ Reduced polymer concentration between the surfaces

• Bulk polymer concentration $\rho$, 

Applying contact value theorem: $P(D) = kT [\rho_s(D) - \rho_s(\infty)]$

Attractive depletion force per unit area between the surfaces at contact

$P(D \rightarrow 0) = -\rho kT$

Depletion free energy per unit area

$W(D \rightarrow 0) \approx -\rho R_g kT$

example) $\rho = 10^{24} \text{ m}^{-3}$, $R_g = 5 \text{ nm}$, $T=25 \text{ °C}$

Interaction energy between two surfaces decrease by 0.2 mJ/m² due to depletion
Strong depletion force
- High bulk concentration of polymer molecule (high $\rho$)
- Large $R_g$ (high MW)

⇒ Choose high polymer concentration (high $\rho$, low MW, low $R_g$)

In the limit of very high $\rho$, low $R_g$
- Adhesive minimum becomes deeper
- Range of depletion force decrease (low $R_g$)
- By the time polymer mole fraction reach unity,
  ⇒ Characteristic of a pure liquid or polymer melt

Attractive depletion force
- Explain colloidal particle coagulation
Non-Equilibrium Aspects of Polymer Interactions

Polymer mediated interaction is not always in equilibrium!

- Solvent has to flow out through the network of entangled polymer coils
- Coils themselves must reorder as they become compressed
- New binding sites and bridges have to be formed
- A certain fraction of polymer molecules may have to enter or leave the gap region altogether

▶ Molecular relaxation mechanisms

- Concerted motions of many entangled molecules
- Require many hours or days (c.f. $10^{-6}$ sec for isolated coils)
- Hysteresis, time-dependent effects
Thermal Fluctuation Forces between Fluid-like Surfaces

- micelles, microemulsion droplets, biological membranes
- constantly changing shapes
- a number of repulsive ‘ thermal fluctuation ’
- protrusion, undulation, peristaltic motion

Thermally mobile or fluid-like surfaces

protrusion  Undulation forces  Peristaltic forces
Approaching two amphiphilic surfaces (molecular - scale overlap)

- protruding segments are forced into the surfaces
- for grafted chain: remain between the surfaces
- for adsorbed chain: forced out into the bulk liquid
Approximation

Energy increase linearly with the distance $z$, that the molecules protrude into the water.

Protrusion energy

$$\sigma(zi) = \alpha_p z_i$$

$(\alpha_p : \text{interaction parameter units, Jm}^{-1})$

The density of protrusion extending distance $z$ from the surface:

$$\rho(0)e^{-\alpha_p z_i / kT} = \rho(0)e^{-z_i / \lambda}$$

$$\lambda = \frac{kT}{\alpha_p} \quad (\text{the protrusion decay length})$$
Protrusion Forces III

- The protrusion force between two amphiphilic surfaces

Lateral dimension $\sigma$

Extending a distance $z_i$ into the solution

Γ protrusion sites per unit area, by potential distribution theorem (Eq. 4.9)

The interaction free energy

$$W(D) = -\Gamma kT \ln \left\{ \int_0^D \int_0^{D-z_1} \exp\left[ -\alpha_p (z_1 + z_2) / kT \right] dz_1 \right\} = -\Gamma kT \ln \left\{ (kT / \alpha_p)^2 \left[ 1 - (1 + D\alpha_p / kT)e^{-\alpha_p D / kT} \right] \right\}$$

Protrusion pressure

$$P(D) = -\partial W / \partial D = \frac{\Gamma \alpha_p^2 D / kT e^{-\alpha_p D / kT}}{[1 - (1 + \alpha_p D / kT)e^{-\alpha_p D / kT}]} = \frac{\Gamma \alpha_p (D / \lambda) e^{-D / \lambda}}{[1 - (1 + D / \lambda)e^{-D / \lambda}]}$$  \hspace{1cm} (14.11)

- $\lambda < D < 10\lambda$

  $$P(D) = 2.7 \Gamma \alpha_p e^{-D / \lambda} \quad (\lambda \approx kT / \alpha_p)$$  \hspace{1cm} (14.12)

- $D < \lambda$

  $$P(D \to 0) = 2\Gamma kT / D$$  \hspace{1cm} (14.13)
Eq. (14.12) corresponds to an energy per unit area

\[ W(D) = 2.7 \Gamma \alpha_p \lambda \, e^{-D/\lambda} \approx 3 \Gamma kT \, e^{-D/\lambda} \quad (14.14) \]

Compare with…

\[ W(D) \approx 36\Gamma kT \, e^{-D/R_s} \quad \text{(end grafted chains)} \]
\[ W(D) \approx 30\Gamma kT (L/s) \, e^{-\pi D/L} \quad \text{(two brush layers)} \]
Undulation and Peristaltic Forces I

**Arise from the entropic confinement** of their undulation and peristaltic waves as two membranes approach each other.

⇒ **Derived from contact value theorem** (entropic force per unit area)

\[ P(D) = kT[\rho_s(D) - \rho_s(\infty)] \]

(\(\rho_s\) : Volume density of molecules in contact with the surfaces)

**Undulation force** - Membrane’s bending modulus, \(k_b\)

In thermally excited waves

The density of contacts

\[ \rho_s(D) = 1/(\text{volume mode}) = 1/\pi^2D \]

\[ \rho_s(\infty) = 0 \]

By the ‘chord theorem’ Eq.(9.7) \(x^2 \approx 2RD\)

The undulation pressure

\[ P(D) = \frac{kT}{\pi^2D} \approx \frac{kT}{2\pi RD^2} \]

Elastic bending energy, \(E_b\) of a curved membrane with local radii \(R_1\) and \(R_2\)

\[ E_b = \frac{1}{2}k_b\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 = 2k_b/R^2 \quad \text{for} \ R_1 = R_2 = R \]
At temperature $T$, suppose that each mode has area $\pi x^2$ & energy $\sim kT$

$$kT \approx 2\pi x^2 k_b / R^2 = 4\pi D k_b / R$$  

**Eq. (14.16)**  
$$P(D) \approx (kT)^2 / k_b D^3$$

Undulation force can be drastically reduced or even eliminated!  
- when a membrane carries a surface charge  
- when it is in tension

**Peristaltic force** - Area expansion modulus, $k_a$

Mean area, $a = \pi x^2$

Exceeding surface area per mode, $\Delta a = \pi D^2$

Elastic energy $E_a$

$$E_a = \frac{1}{2} K_a \frac{(\Delta a)^2}{a} = \frac{\pi k_a D^4}{2x^2} \quad (14.19)$$

The peristaltic pressure

$$P(D) = kT / \pi x^2 D \approx \frac{2(kT)^2}{\pi^2 k_a D^2} \quad (14.20)$$