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ON THE STATISTICAL THERMODYNAMICS OF MEMBRANE FORMATION

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Modifying a procedure developed by Scheutjens and Fleer (J. Phys. Chem. 83 (1979) 1619; J. Phys. Chem. 84 (1980) 178) to describe adsorption of polymers, a lattice theory is proposed to formulate the formation and properties of amphiphilic bilayer membranes. In this theory individual conformations are distinguished and lateral interactions are taken into account in a Flory-Huggins approximation. Probability distributions of head, tail and solvent segments are computed and it is shown that they are not narrow, i.e., membrane properties are subject to considerable fluctuations. The average concentration of the water in the hydrophobic core is nonzero. Various extensions, consequences and applications are proposed.

1. Introduction

One of the most important biological properties of membranes is their ability to act as a selective transport medium. Carrier transfer and dissolution of foreign substances in membranes are phenomena for which ultimately an interpretation must be sought in terms of the statistical properties of the membranes. For this reason, the description of the ordering, fluctuations in composition and the conditions under which a membrane is stable, in the presence or absence of admixtures, are important statistical thermodynamical challenges.

The present paper proposes a theory for the formation and description of membranes of amphiphilic molecules whereby also the distributions of the head groups and solvent molecules are considered. Despite a number of simplifying assumptions this theory is able to describe essential features of stability and composition. Basically, it is a lattice theory in which interactions are accounted for between three types of groups: solvent molecules (o), hydrocarbon chain segments (a) and head groups (b). The (Helmholtz) free energy is computed of a solution of the amphiphatic molecules (a,b) in the solvent o and conditions are formulated under which a bilayer forms spontaneously. Also, the composition of this bilayer is computed.

Our approach has a more a priori character than the statistical theory of Gruen [1], based on a model put forward by Marčelja [2], describing the statistical properties of one molecule in the bilayer in a canonically averaged surrounding of the other molecules, and it is complementary to molecular dynamical simulations [3].

2. Basic ideas

The main problem is to formulate the free energy of a solution of a,b molecules in solvent o as a function of composition and obtain conditions under which the system exhibits spontaneous phase separation to form bilayer structures. This issue is similar to that of the formation of other

types of aggregates, such as micelles, vesicles and liposomes, phenomena that can also be tackled by our theory, but that will not be discussed now. As it is our purpose to describe not only the average properties of the membranes obtained, but also the fluctuations around those averages, it is mandatory to formulate the probabilities of specific conformations.

A theory satisfying this requirement is the polymer adsorption theory, developed recently in our laboratory by Scheutjens and Fleer (SF theory) [4a,4b], a lattice theory, that we shall use here. Alternatively, the analysis could be based on the theory by Levine et al. [5], having essentially the same properties. The adsorbent is flat and contains L lattice sites; in the solution there are parallel layers, each again of L sites, numbered $i = 1$ (adjacent to the surface) to $i = M$ (bulk solution). Each solution site can be occupied by either a solvent molecule (o) or a polymer segment (a). The original theory considers only homopolymers. It is a special feature of the theory that it discriminates between different conformations, which are considered fully defined by specifying the layer i in which each segment of rank s is found. Fig. 1 illustrates this definition for an amphiphilic molecule. If z is the co-ordination number of the lattice, the degeneracy of each conformation is $Lz^{r-1}\,\omega$, where

$$\omega = \lambda_0^q \lambda_1^{r-1-q} \tag{1}$$

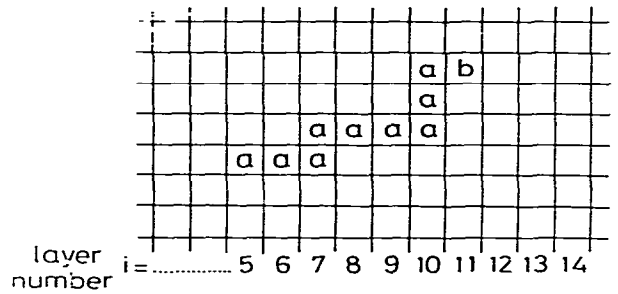

Fig. 1. The conformation of the amphiphilic molecule a_9b in a lattice is defined by specifying in each layer i the rank s of the segment. In this example it is given as (5,1), (6,2), (7,3), (7,4), (8,5), (9,6), (10,7), (10,8), (10,9), (11,10). The degeneracy is $\lambda_0^3\lambda_1^6$.

In eq. 1 r is the total number of segments, q the number of bonds parallel to the surface and $r-1-q$ the number of bonds from i to $(i+1)$ or $(i-1)$. In the example $r=10$ and $q=3$. The quantities λ_0 and λ_1 are lattice structure parameters: λ_0 is the fraction of steps possible inside i and λ_1 is the same for steps from i to $(i+1)$ and for steps from i to $(i-1)$. For a cubic lattice $\lambda_0 = 4/6$ and $\lambda_1 = 1/6$, for a hexagonal one $\lambda_0 = 6/12$ and $\lambda_1 = 3/12$. Always $\lambda_0 + 2\lambda_1 = 1$.

The original theory ignores size differences between polymer segments and solvent molecules and allows step reversal, the latter simplification being partly compensated by counting all probabilities with respect to the bulk as the reference state, where step reversal is also allowed.

The probability of the various conformations is not only determined by eq. 1 but also by segment-segment and segment-solvent interactions. In this connection it appears expedient to define free segment probabilities P_i^a as the probability of finding an a segment in layer i, if it is entirely free; i.e., if it is not bound covalently to other segments. Free segment probabilities are virtually weighting factors.

Lateral interactions are accounted for in a mean field approximation: in each site of, say, layer i the interaction energy of the segment (or solvent) molecule in it was considered to be determined by the Flory-Huggins (FH) interaction parameter χ_{ao} and the average volume fraction of solvent molecules $\langle\phi_i^o\rangle$ (or polymer segments $\langle\phi_i^a\rangle$) around that site

$$u_{ao,i} = kT\chi_{ao}n_i^a\langle\phi_i^o\rangle = kT\chi_{oa}n_i^o\langle\phi_i^a\rangle \tag{2}$$

where k is Boltzmann's constant, T the absolute temperature and n_i^a and n_i^o the numbers of polymer segments and solvent molecules in i, respectively. The quantity $\langle\phi_i^a\rangle$ in eq. 2 is composed of a fraction λ_0 'in-layer' contacts, λ_1 contacts with layer $(i-1)$, and λ_1 with layer $(i+1)$. If the volume fractions in each layer are defined through $\phi_i^a = n_i^a/L$, $\phi_i^o = n_i^o/L$, etc., then

$$\langle\phi_i^a\rangle = \lambda_1\phi_{i-1}^a + \lambda_0\phi_i^a + \lambda_1\phi_{i+1}^a \tag{3}$$

and similarly for $\langle\phi_i^o\rangle$.

In applying SF theory to the association of

amphiphilic molecules of type $a_r b$ two modifications must be introduced.

First, as there are now three materials that can occupy a site (chain segment a, head group b, or solvent molecule o), three FH interaction parameters are needed: χ_{ao}, χ_{bo} and χ_{ab}. (By virtue of the definition of these parameters $\chi_{aa} = \chi_{bb} = \chi_{oo} = 0$.) The interaction energy in layer i now contains three terms of the type of eq. 2:

$$u_{\text{int},i} = kT\left[\chi_{ao} n_i^a \langle \phi_i^o \rangle + \chi_{bo} n_i^b \langle \phi_i^o \rangle + \chi_{ab} n_i^a \langle \phi_i^b \rangle\right] \tag{4}$$

The second and more principal difference is that in the present case there is no adsorbent , a feature which has two consequences. The first is of a physical nature: instead of the binding energy of segments with the surface it is now the mutual attraction between chain segments that is responsible for the formation of a membrane. The second is of a mathematical character: some procedure must be found to fix spatially the position of the membrane to be formed, without making a priori statements about its composition. For instance, we do not want to fix the positions of the head groups (as has been done for instance in refs. 1 and 3), and since there is some spread among these positions because of spontaneous fluctuations. This problem was solved by locating the lattice on the membrane to be generated, which is mathematically equivalent to having reflecting boundaries half way in the membrane. This implies that symmetry of the membrane is anticipated, i.e., the probabilities of given conformations are identical on the two sides of the membrane. More specifically, i is counted from the heart of the membrane upward or downward, in principle running infinitely far, but in fact until some layer $+M$ or $-M$ where bulk properties are reached.

It may be added that the chosen lattice symmetry leads to the formation of membrane-like bilayer structures, but that other choices could have been made that would have led to, say, micellar or cylindrical associates. In fact, the free energies of the various aggregative structures could in this way be compared and hence the relative stability domains established, but this elaboration is beyond the scope of the present paper.

Finally, both the original SF theory and the present elaboration have in common that the equilibrium distribution is obtained by maximizing the canonical partition function with respect to the numbers of the various possible conformations. The iteration is started by letting the computer bring about a membrane-like perturbation in the composition; under conditions where the membrane is stable these perturbations grow in successive steps, whereas below a certain threshold value they disappear spontaneously. In the present analysis, a constant bulk composition was assumed, which virtually means that the solution volume is large with respect to that of the membrane.

3. Segment probabilities

Details of the membrane structure are obtainable by modifying SF theory. These are expressed in two characteristic quantities, the free segment probability P_i^x, which has been defined before, and the end segment probability $P^x(i,r)$ of material x, which is the probability of finding the last segment of an r-mer in layer i (x = a or b). Obviously, $P^x(i,1) = P_i^x$.

The probability of finding individual conformations is directly coupled to P_i^a and P_i^b. The derivation of this relationship is similar to that in the SF theory (the differences being that in the membrane case no adsorption energy occurs and that amphiphilic molecules contain two types of segments) and runs as follows.

The ratio between the canonical partition function $Q(M,L,T,\vec{n}_c)$ for a set of conformations $\vec{n}_c$, and the same for a reference system consisting of pure solvent and a pure amorphous amphiphilic phase, reads as follows

$$Q = \frac{\Omega}{\Omega_+} \exp[-(U - U_+)/kT] \tag{5}$$

with

$$U = \sum_i u_{\text{int},i} \tag{6}$$

$u_{\text{int},i}$ being given in eq. 4 and

$$U_+ = kT\chi_{ab}\sum_i n_i^a \phi_+^b = kT\chi_{ba}\sum_i n_i^b \phi_+^a \tag{7}$$

the subscript + always referring to the reference state defined above, i.e., for an $a_r b$-type molecule

$\phi^{b}_{+} = (t+1)^{-1}$ and $\phi^{a}_{+} = t/(t+1)$. The degeneracy of the system Ω is related to the quantity ω_c of a specified conformation c (defined through eq. 1 with $q = q_c$) through [4a]

$$\Omega = (L!)^{\mathcal{M}} \left(\frac{z}{L}\right)^{(r-1)n} \prod_c \frac{\omega_c^{n_c}}{n_c!} \prod_i \frac{1}{n_i^{o}!} \tag{8}$$

where z is the coordination number of the lattice, n_c the number of conformations c, and $n = \sum_c n_c$ the total number of chains. An expression for Ω_+ has been derived by Flory [6]:

$$\Omega_+ = \frac{(rn)!}{n!}\left(\frac{z}{rn}\right)^{(r-1)n} \tag{9}$$

Eqs. 5–9 give Q at fixed $\vec{n}_c$. The corresponding equilibrium situation is obtained by maximizing Q with respect to the number of conformations. Or, for that matter, we want to find the number n_d of chains in a particular conformation d in the equilibrium state. From thermodynamics

$$\left(\frac{\partial F}{\partial n_d}\right) = -kT\left(\frac{\partial \ln Q}{\partial n_d}\right)_{\mathcal{M},L,T,n_{c\neq d}} = \mu(\text{chain}) - r\mu^{o} \tag{10}$$

represents the free energy change of substituting r solvent molecules by one chain of length r, and at equilibrium this change is a constant determined by the choice of the reference state. The differentiation is carried out similarly to that in the SF theory, the only difference being that the chain contains a and b segments (for an a,b-type molecule $t+1 = r$). The result is

$$n_d = LC\omega_d \prod_i (P_i^{a})^{r^{a}_{i,d}} (P_i^{b})^{r^{b}_{i,d}} \tag{11}$$

with

$$\ln P_i^{a} = \chi_{aa}(\langle\phi_i^{a}\rangle - \langle\phi_i^{o}\rangle) + \chi_{ba}\langle\phi_i^{b}\rangle + \chi_{ab}(\phi^{b}_{+} - \langle\phi_i^{b}\rangle) + \ln\phi_i^{o} \tag{12a}$$

$$\ln P_i^{b} = \chi_{ba}(\langle\phi_i^{b}\rangle - \langle\phi_i^{o}\rangle) + \chi_{aa}\langle\phi_i^{a}\rangle + \chi_{ba}(\phi^{a}_{+} - \langle\phi_i^{a}\rangle) + \ln\phi_i^{o} \tag{12b}$$

$$rC = \exp\{(\mu(\text{chain}) - r\mu^{o})/kT\}\exp(r-1) \tag{13}$$

where $\langle\phi_i^{a}\rangle$, etc., is defined in eq. 3 and ω in eq. 1; $r^{a}_{i,d}$ is the number of segments of type a that conformation d has in layer i ($r^{a}_{i,d} = (\partial n_i^{a}/\partial n_d)n_{c\neq d}$, etc.). The quantities P_i^{a} and P_i^{b} are the free segment probabilities, discussed before.

For various purposes it is expedient to rescale these probabilities by referring them to the corresponding bulk solution values P^{a}_{*} and P^{b}_{*}, that are obtained by substituting ϕ^{a}_{*} for $\langle\phi_i^{a}\rangle$ and ϕ^{b}_{*} for $\langle\phi_i^{b}\rangle$ in eq. 9. Defining this rescaled probability as

$$p_i^{a} = P_i^{a}/P^{a}_{*} \tag{14}$$

then

$$p_i^{a} = \frac{\phi_i^{o}}{\phi^{o}_{*}} e^{\chi_{aa}(\langle\phi_i^{a}\rangle - \langle\phi_i^{o}\rangle)} e^{\chi_{ab}(\phi^{o}_{*} - \phi^{a}_{*})} e^{(\chi_{ba} - \chi_{ab})(\langle\phi_i^{b}\rangle - \phi^{b}_{*})} \tag{15}$$

and similarly for p_i^{b}.

The end-segment probability (also rescaled to $p(i,r) = P(i,r)/P(*,r)$) is an important characteristic because it expresses the spatial distribution of the chains in the membrane. This probability can be found from that of a single segment by generating the chain in the lattice, considering the lattice parameters (λ_0 and λ_1) and the free segment probabilities in each layer. Thus, using the recurrent expression [4a,4b,7]

$$p(i,r) = p_i[\lambda_1 p(i-1,r-1) + \lambda_0 p(i,r-1) + \lambda_1 p(i+1,r-1)] \tag{16}$$

$p(i,r)$ is related to p_i and three end-segment probabilities of chains that are one segment shorter. In turn, these end-segment probabilities can be converted into those of chains with length $(r-2)$, using the same equation, and the procedure can be repeated till the last segment, for which $p(i,r) = p_i$. This way of generating a chain can be written as a matrix multiplication

$$\begin{pmatrix} \vdots \\ p(-1,r) \\ p(1,r) \\ p(2,r) \\ \vdots \\ p(i,r) \\ \vdots \end{pmatrix} = \begin{pmatrix} -\lambda_1 p^{x}_{-1} & \lambda_0 p^{x}_{-1} & \lambda_1 p^{x}_{-1} & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \lambda_1 p^{x}_{1} & \lambda_0 p^{x}_{1} & \lambda_1 p^{x}_{1} & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \lambda_1 p^{x}_{2} & \lambda_0 p^{x}_{2} & \lambda_1 p^{x}_{2} & \cdots & \cdots & \cdots \\ & & & & & & & \\ & & & & & \lambda_1 p_i^{x} & \lambda_0 p_i^{x} & \lambda_1 p_i^{x} \end{pmatrix} * \begin{pmatrix} \vdots \\ p(-1,r-1) \\ p(1,r-1) \\ p(2,r-1) \\ \vdots \\ p(i,r-1) \\ \vdots \end{pmatrix} \tag{17}$$

formally abbreviated to

$$\vec{p}(r) = \vec{\vec{W}}^{x}\vec{p}(r-1) \tag{18}$$

whether or not $\vec{\vec{W}}^{x}$ is $\vec{\vec{W}}^{a}$ or $\vec{\vec{W}}^{b}$ depends on the composition of the molecule and on which side the generation starts. For homopolymers all matrices are identical and $(r-1)$ multiplications are needed. Execution of the matrix multiplications leads to a set of end-segment probabilities that can again be represented by a matrix and has either this shape

$$\vec{\vec{p}} = \begin{pmatrix} \vdots & & \vdots & & \vdots \\ p(-1,1) & \cdots & p(-1,s) & \cdots & p(-1,r) \\ p(1,1) & & p(1,s) & & p(1,r) \\ p(2,1) & & p(2,s) & & p(2,r) \\ \vdots & & \vdots & & \vdots \\ p(i,1) & \cdots & p(i,s) & \cdots & p(i,r) \\ \vdots & & \vdots & & \vdots \end{pmatrix} \tag{19a}$$

or this

$$\vec{\vec{p}}_{inv} = \begin{pmatrix} \vdots & \vdots & & \vdots \\ p_{inv}(-1,1) & p_{inv}(-1,s) & \cdots & p_{inv}(-1,r) \\ p_{inv}(1,1) & p_{inv}(1,s) & & p_{inv}(1,r) \\ p_{inv}(2,1) & p_{inv}(2,s) & & p_{inv}(2,r) \\ \vdots & \vdots & & \vdots \\ p_{inv}(i,1) & p_{inv}(i,s) & & p_{inv}(i,r) \\ \vdots & \vdots & & \vdots \end{pmatrix} \tag{19b}$$

depending on the end of the molecule where the multiplication has started. In eqs. 19 s indicates the rank of the segment in the chain, in eqs. 19a and 19b counted from different sides. For homopolymers $\vec{\vec{p}} = \vec{\vec{p}}_{inv}$.

4. Segment distributions

The ultimate goal is to obtain the values ϕ_1^a, $\phi_2^a \ldots$, $\phi_i^a \ldots$ and ϕ_1^b, $\phi_2^b \ldots$, $\phi_i^b \ldots$ In each layer i all volume fractions $\phi_i^x(s)$ of all segments with rank s must be summed, both for $x = a$ and $x = b$. To that end it is convenient to define $p(s,i;r)$ as the probability (with respect to bulk) that segment s of an r-mer is found in layer i. Scheutjens and Fleer [4a] showed that

$$p(s,i;r) = p(i,s)\,p_{inv}(i,r-s+1)/p_i \tag{20}$$

As stated, for homopolymers $p = p_{inv}$. The physical meaning of eq. 20 is that the probability of finding for each conformation the s-th segment of an r-mer in layer i is equal to the product of the probability that, starting from one side, after $s-1$ steps layer i is reached and the probability that, coming from the other side, layer i is reached after $(r-s)$ steps. The weighting factor p_i enters because segment s is counted twice. As both for $x = a$ and $x = b$ $p(s,i;r) = r\phi_i(s)/\phi_*$, we can write, discriminating between segments of types a and b

$$\phi_i^a(s) = \frac{\phi_*}{r} p(s,i;r)\,\delta_{x(s),a} \tag{21a}$$

$$\phi_i^b(s) = \frac{\phi_*}{r} p(s,i;r)\,\delta_{x(s),b} \tag{21b}$$

Combining eqs. 20 and 21, the total values ϕ_i^a and ϕ_i^b can be obtained by summing over r

$$\phi_i^a = \frac{\phi_*}{r p_i^a} \sum_{s=1}^{r} p(i,s)\,p_{inv}(i,r-s+1)\,\delta_{x(s),a} \tag{22a}$$

$$\phi_i^b = \frac{\phi_*}{r p_i^b} \sum_{s=1}^{r} p(i,s)\,p_{inv}(i,r-s+1)\,\delta_{x(s),b} \tag{22b}$$

Proceeding in this way, one not only obtains the total volume fraction of either type of segment in each layer but it is also possible to discriminate between the segments of differing rank.

Together with ϕ_i^o (which must satisfy the boundary condition $\phi_i^a + \phi_i^b + \phi_i^o = 1$) these are the $3M$ unknowns that have to be computed. This requires iterations, since through eqs. 22 and 18 these unknowns are related to $\vec{p}(r)$ which in turn through eqs. 15 and 3 depends on these unknowns.

Some relevant mathematical aspects are collected in the appendix.

5. Results and discussion

The theoretical picture developed above is very versatile and several important membrane properties can be computed. In addition, it can be the starting point for the description of more complicated systems. Deferring such extensions, we

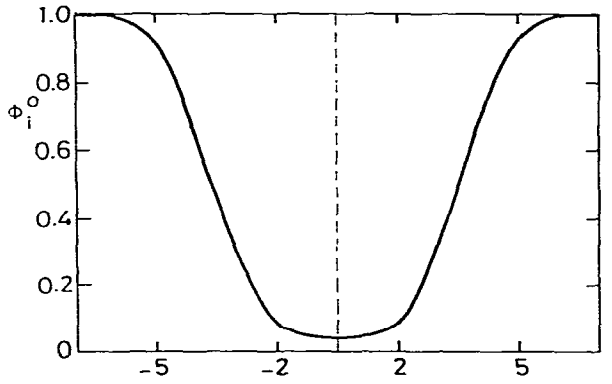

Fig. 2. The water content of symmetrical a_9b_2 membranes. $\chi_{ao} = \chi_{ab} = 2.5$. $\chi_{bo} = -0.5$. $\phi_* = 10^{-4}$. Size of head group = 2 lattice sites, hexagonal lattice.

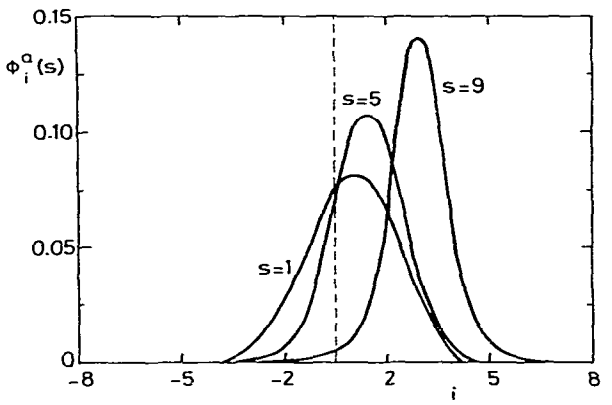

Fig. 4. Distribution of chain segments a of different rank s. Conditions as in previous figures. s is counted from the tail end. (To avoid overcrowding of the figure, only chains ending with their head group at the right-hand side are counted.)

shall now give some results for simple systems that are mainly meant as illustrations.

In these first examples the lattice is hexagonal and we reduced the three FH parameters to two by letting $\chi_{ao} = \chi_{ab}$. The molecule is the undecamer a_9b_2, i.e., the head group is twice as large as solvent molecules or tail segments. The doubling of the size of the head group is accomplished by replacing p_i^b by $(p_i^b)^2$ and adjusting the normalization of the volume fractions.

The stability of a membrane is a result of either the attraction between chain segments or the expulsion of chain segments from the solvent (henceforth called 'water'). In order to mimick physical reality we chose χ_{ao} positive and χ_{bo} negative, i.e., the chain segments are repelled but the head groups attracted by the water. Attractive values for the a-o interaction would of course not lead to phase separation.

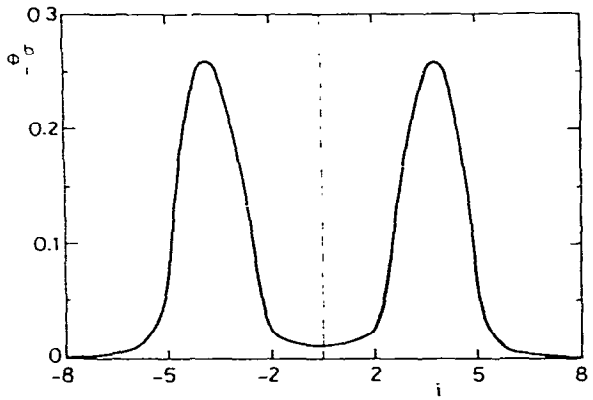

Fig. 3. Head group distribution in a symmetrical a_9b_2 membrane. Parameters as in fig. 2.

Fig. 2 gives the water content of the membrane. The figure shows that the heart of the membrane is by no means devoid of water. In fact, that would be entropically very unfavourable. In view of this, it must also be expected that there is some water in the hydrophobic core of micelles. Obviously, this observation is very relevant for the interpretation of transport through membranes.

The profile of the head segments is represented in fig. 3. This figure shows in the first place that the thickness of a membrane is not a statical but a statistical quantity. Similar reasoning must mutatis mutandis apply to micelles and to soap films, a feature that has been largely ignored in analyses involving such aspects as the thickness of stagnant adjacent water layers or charge distributions. It follows also from fig. 3 that the head groups are not meticulously arranged in the same plane but display considerable statistical spread, and their concentration in the heart is nonzero. The computations show that under the conditions chosen the

volume fraction ϕ_i^b never exceeds 0.23, hence there is plenty of room for water molecules and chain segments between them. In line with this, it must be anticipated that also in micelles there are several contacts between water molecules and the methylene groups of the chain, especially those close to the head group, a feature for which experimental evidence has been collected [8,9]. Even inside the heart of the membrane the concentration of head groups is not entirely zero; this observation is relevant for estimating the 'flip-flop' rate.

Distributions of chain segments of various rank s are represented in fig. 4. Segments at the beginning of the chain ($s = 1$) enrich largely the centre and have a relatively wide distribution. The further on in the chain, the more the trend to assume a binodal distribution with the penultimate chain element ($s = 9$, i.e., the one adjoining the head group b_2) having a distribution resembling that of the head group. Such distributions can be used to estimate the ordering parameter which, in turn, is measurable by ESR and NMR [10].

Fig. 5 gives some impression of the membrane composition and stability domain. The excess matter with respect to bulk is defined through

$$\theta = \sum_{i=-M}^{M} \left(\phi_i^a + \phi_i^b - \phi_*^a - \phi_*^b\right) \qquad (21)$$

This parameter is also a measure of the membrane thickness expressed as the number of layers.

There is a relatively large range of ϕ_* where the membrane is stable and where the composition is relatively insensitive to the bulk concentration. The affinity of the head group toward the solvent, characterized through χ_{bo}, has little effect on these features, although a more negative value tends to enlarge the stability range of the bilayer. To the left so little material is available that membranes cannot remain stable. On the other hand, to the right, i.e., at high volume fractions, the membrane tends to grow into other than bilayer structures, first into multilayers, till at still higher ϕ_* full phase separation ensues. It is striking that the thickness is much less than twice the extended chain length. It is important to note that this is essentially due to the statistical nature of this quantity and that it is not necessary to invoke chain tilting as an explanation.

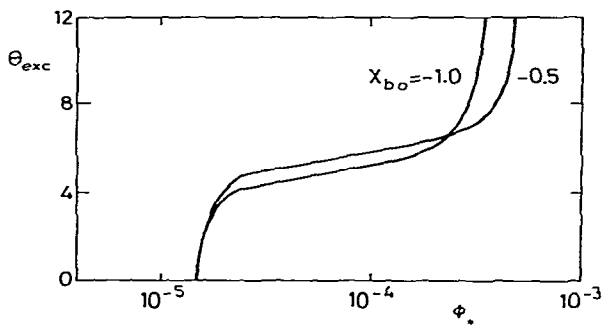

Fig. 5. The excess material accumulated in the membrane, a measure of the membrane thickness expressed in number of lattice layers. Parameters as in previous figures. χ_{bo} is indicated.

The above examples served as illustrations and are by no means exhaustive. The picture can be readily extended to include more systematically the effects of variables such as the chain length, interaction parameters and size of the head group. Of the various extensions one could think of: variation of the shape of the head group and the number of chains per head group (to mimick lipids), adding a third component (mimicking a carrier), considering other associative structures (stratified membranes, micelles, vesicles) and accounting for electrical double layers.

6. Conclusion

It was shown that the statistical framework, developed by Scheutjens and Fleer to describe the adsorption of polymers, can be modified to obtain conditions for formation and properties of bilayer membranes of amphiphilic substances. Numerous extensions and applications are envisaged. Several of our findings may, mutatis mutandis, be applicable to micelles, soap films and other associative structures. Especially the statistical character of a membrane structure was borne out.

Appendix

The implicit equations in ϕ_i^o, ϕ_i^a and ϕ_i^b are solved as follows. The boundary condition $\phi_i^o + \phi_i^a$

$+\phi_i^b = 1$ is used to reduce the number of variables by one per layer.
Define

$$\nu_i^b = \phi_i^b/(\phi_i^a + \phi_i^b) \tag{A1}$$

and substitute $(1-\phi_i^o)(1-\nu_i^b)$ for ϕ_i^a and $(1-\phi_i^o)\nu_i^b$ for ϕ_i^b in eq. 15:

$$\ln p_i^a = \chi_{ao}\left(\langle(1-\phi_i^o)(1-\nu_i^b)\rangle - \phi_i^o + \phi_s^o - \phi_s^a\right) + (\chi_{bo}-\chi_{ab})\left(\langle(1-\phi_i^o)\nu_i^b\rangle - \phi_s^b\right) + \ln(\phi_i^o/\phi_s^o) \tag{A2}$$

$$\ln p_i^b = \chi_{bo}\left(\langle(1-\phi_i^o)\nu_i^b\rangle - \phi_i^o + \phi_s^o - \phi_s^b\right) + (\chi_{ao}-\chi_{ab}) \times \left(\langle(1-\phi_i^o)(1-\nu_i^b)\rangle - \phi_s^a\right) + \ln(\phi_i^o/\phi_s^o) \tag{A3}$$

If we place a mirror between layer $i=-1$ and layer $i=1$, we have $\phi_{-i}^o = \phi_i^o$ and $\nu_{-i}^b = \nu_i^b$. Thus, only $2M$ equations in $2M$ unknowns remain to be solved by some standard method, where M is sufficiently large so that layer M is in the bulk solution. For instance, if the Fortran program of Powell [11] is used the unknowns ϕ^o and ν^b are equivalent to $2M$ iteration variables x_i:

$$\phi_i^o = x_{2i-1}\ \nu_i^b = x_{2i} \tag{A4}$$

and the $2M$ functions f_i for which a zero is to be found are given by

$$f_{2i-1} = \phi_i^a - (1-\phi_i^o)(1-\nu_i^b)$$
$$f_{2i} = \phi_i^b - (1-\phi_i^o)\nu_i^b \tag{A5}$$

where ϕ_i^a and ϕ_i^b are computed via eqs. 22a and b.

It is important to keep $0 < x_i < 1$. This can be done by choosing a good initial guess for x_i and a small limit for the step size per iteration. If ϕ_t is some threshold value (≈ 0.4) for the volume fraction of segments in the membrane, starting values satisfying

$$x_1 = x_3 < 1-\phi_t$$
$$x_{2i-1} = 1-\phi_* \ (i>2)$$
$$x_{2i} = 1/r$$

will be adequate. For double-sized head groups the starting values x_{2i} are set to $2/(r+1)$.

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