Boundary effects in the hexagonal packing of rod-like molecules inside a right circular cylindrical domain. I. The case of right circular spherocylindrical molecules

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We derive an upper limit, imposed by kinematic constraints, for the ratio of the average density function relative to the local density function for a freely rotating right circular cylindrical domain made of right circular spherocylindrical molecules. The derivation is made under the assumption that the molecules are rigid, that they are close packed and that their molecular axes are perpendicular to the base of the domain. For domains containing more than 100 molecules, the average density, evaluated as a function of domain size, is well approximated by a simple smooth analytical expression. For smaller domains, on the other hand, the boundary effects lead to an average density that varies erratically with the size of the domain. The contribution of the boundary effects to the difference between the local density on the average domain density, increases with decreasing domain size. It is negligible for very large domain, it is about 2.5% for domains containing around 10 000 molecules, and it can be as high as 20% for very small domains. The theoretical results obtained here are consistent with the reported discrepancy between the value of the molecular area obtained from pressure area measurements and that obtained from X-ray measurements.

1. Introduction

As physicists and biophysicists tackle living systems a new level of complexity has to be dealt with. Living systems are far from the traditional two body scattering problem of particle physics on the one hand, and do not have the high degree of symmetry characteristic of large, many body, crystalline systems on the other hand. To understand a living system, we have to study it at different levels simultaneously. We have to study it: (i) at the molecular level; (ii) at the level of intermediate subsystems; and (iii) globally as an integrated whole. Consequently, we have to deal with more than one scale at a time, and this is one of the main difficulties encountered in studying living systems from a theoretical point of view.

When we study a system at one scale, we can, and usually do, ignore boundary

effects. On the other hand, when we are studying a system at two scales simultaneously, the boundaries of the smaller scale are important features of the building blocks of the larger scale. Consequently, problems that were previously solved ignoring boundary conditions, have to be reinvestigated.

One such multiscale problem arises in studying the molecular organization of Langmuir films at the gas-liquid interface [16]. In one of the simplest cases, molecules are taken to be rod-like and are modeled by spherocylinders: right circular cylinders [7] supplemented by two hemispheres, one at each of the two ends of the molecule [1]. The molecules are grouped together in domains and the film is made up of a large number of such domains [3,5,9,10,13,15]. The domains tend to be circular [2,11,12,14]. Thus, depending on the scale at which we measure, we have three different densities: (i) the average density of a single molecule; (ii) the average density of a domain; and (iii) the average density of the monolayer (or film). Dutta et al. [6] have already noted an apparent discrepancy between the X-ray and the pressure area determinations of the "molecular area" of lead stearate and lignoseric acid films at the gas-liquid interface.

By studying the molecular organization of ultrathin films we can establish a relation between the average film density, and the average molecular density, thus obtaining a relation between molecular parameters and macroscopic measurements. At the heart of this organisational problem we encounter the geometrical problem of close packing of rod-like (right circular cylindrical) molecules into a large right circular cylindrical domain. For vertically oriented molecules, this can be reduced to the problem of close packing of small disks into a large circle.

When we first encountered the above packing problem, while studying molecular organization in Langmuir films, we took it for granted that the problem had already been worked out. Therefore, we set out on a literature search to find the result and use it in our study. However, we fast realized that close packing and tiling problems had invariably been solved for volumes and surfaces of infinite extension thus neglecting boundary effects.

In this paper we study the organizational problem of close packing of vertically oriented rod-like molecules inside a right circular cylindrical domain while taking boundary effects into account. We then use the results to evaluate the importance of these boundary effects in determining the value of the relative average density inside the domain (average domain density over average molecular density), as a function of the relative size of the domain (domain cross-sectional area over molecular cross-sectional area).

This paper is the first in a series studying theoretically the molecular organization and molecular dynamics in ultra-thin films at the gas-liquid interface in view of developing a global detailed dynamic molecular model. The first phase of the study is concerned with the determination of the simplest film parameter: the ratio of the average film density to the average molecular density.

Static studies, establishing the basic geometrical structure of molecular organization, are a reasonable starting point and provide upper bounds on the relative average density of the film. In the static problem we have to deal with the organization of

molecules within a domain, and the organization of domains within a film. The first paper in this series will deal with the former aspect.

The molecules within a domain are all parallel to each other and may have any collective orientation relative to the interface. The simplest orientation to study is when the molecular axes are perpendicular to the interface, and in the present paper we restrict our attention to this special case.

The paper is written with the ultimate objective of the study in mind. Consequently, the definitions and symbols are chosen to be useful for the study of the structure of ultra thin films in general, and for the study of their relative (ratio of domain to molecular) average density in specific. Thus, rather than define the problem in its most restrictive sense, the notation we use in certain instances will be more general than strictly needed for the purpose of this paper. This generality will serve to remind the reader of the context in which the derivation is made and to put the paper in perspective. This generality also serves to establish a certain uniformity throughout the series of papers in as far as notation and definitions are concerned.

In figure 1, for instance, the angle θ is introduced even though in this paper we will only deal with the case $\theta = 0$. Furthermore, the spherocylindrical model of the molecules is introduced even though the two end hemispheres do not influence the calculation as long as $\theta = 0$. In this limiting case, only the rod-like character of the molecular model matters. Similarly, we will introduce the so called "half-way plane" of the domain, eventhough for $\theta = 0$ the symmetry properties of this plane are not unique, and its usefulness will only become apparent when we go on to the more general case of inclined molecules.

2. The model

The mathematical problem we have at hand is that of the close packing of parallely oriented right circular spherocylindrical (rod-like) molecules into a larger right circular cylindrical (barrel-like) domain.

2.1. The three dimensional model

2.1.1. The molecules

The molecules are modeled as spherocylinders [1]: that is, they are right circular cylinders capped by two hemispheres one at each end as shown in figure 1. The cylinders have radius r_0 and height h. The hemispheres have radius r_0. Thus the total length d of a molecule is given by

$$d = h + 2r_0 \tag{1}$$

and its cross sectional area σ_0 is
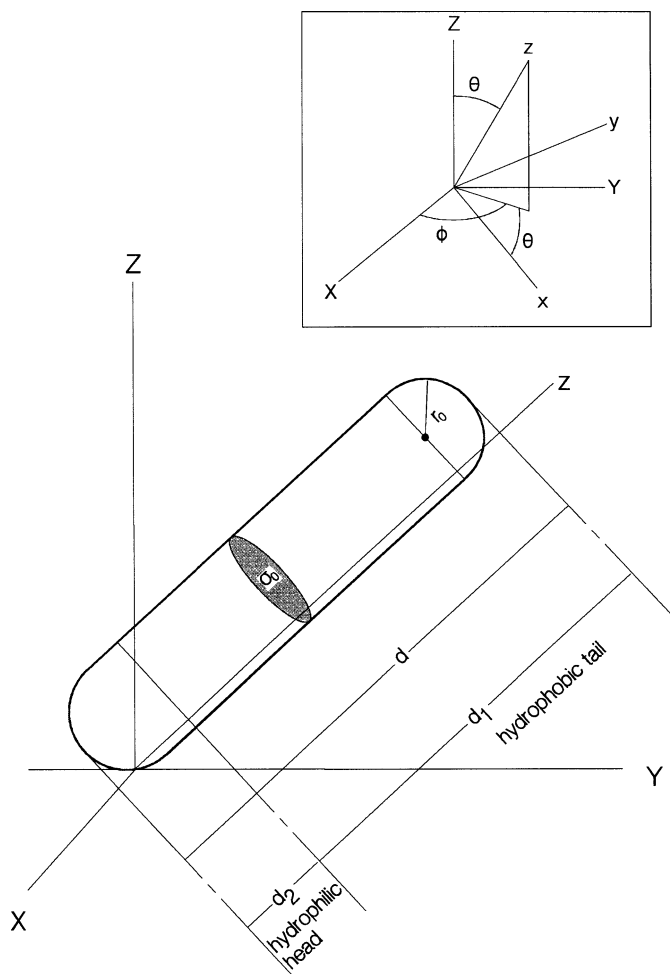
$$\sigma_0 = \pi r_0^2. \tag{2}$$

Figure 1. Model of the rod-like spherocylindrical molecule with its molecular parameters.

The spherocylindrical rod-like model is reasonably realistic for single chain lipid molecules with small polar heads. In fact, as these molecules rotate and vibrate, their atoms do fill a more or less spherocylindrical volume. Since the phenomena we are interested in (pressure-area measurements, X-ray measurements, ellipsometric measurements, etc.) are at a time scale that is large compared to the molecular rotational and vibrational time scales, then the average smeared out atomic cloud produces a spherocylindrical molecule with a certain averaged molecular density.

2.1.2. The domains

Let the number of molecules in the domain under consideration be N. The molecules are assumed to be all identical and they are aligned parallel to each other. This collective parallel alignment of the molecules is the defining characteristic of the
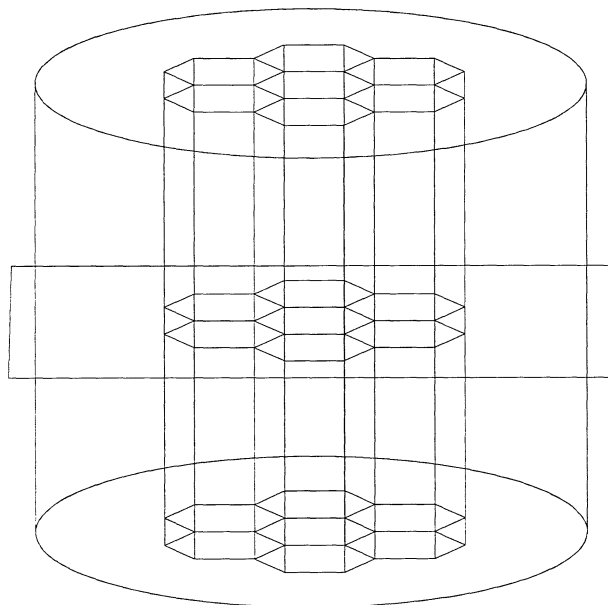
Figure 2. Hexagonal close pack of spherocylindrical molecules in a right circular cylindrical domain: the half-way plane.

domain. We refer to this group of N parallel molecules as the "physical domain". Due to the dimensions of single chain lipid molecules and the number of molecules in a domain, these physical domains are generally rather flat. In general the N molecules will be collectively inclined at an angle θ to the vertical (the normal to the gas–liquid interface), as shown in figure 1. But in this paper we treat only the case of vertically oriented molecules, that is the case when $\theta = 0$, as shown in figure 2.

The boundary of the "physical domain" is rough and toothed. But as the "physical" domain rotates, it will, more or less, sweep a right circular cylindrical volume that we refer to as the "circumscribing domain" or simply as the domain. Thus the domain is modeled as a right circular cylinder enveloping the N molecules of the "physical domain", and with the axis of the cylinder perpendicular to the gas–liquid interface. The radius R and height H of the domain are determined by the condition that R and H be as small as possible consistent with the above mentioned constraints. Thus the height of the cylinder is determined by the inclination of the molecules relative to the interface:

$$H = 2r_0 + h\cos\theta. \tag{3}$$

As for the radius R, it is equal to half the largest dimension of the projection of the "physical domain" on the interface. For the case of vertically oriented molecules, this projection is identical to any horizontal cross-section of the "physical domain".

2.1.3. The half-way plane

The plane perpendicular to the symmetry axis of the domain and situated half-way between the base and the top is referred to as the *half-way plane*. This is the plane in which we will work. The cross-section of the domain in the half-way plane is a disc of radius R. This is the disc on which we will close pack molecular cross-sections. The symmetry axis of the domain passes through the center of this disc. This is the point that we will take as the origin of the coordinates. The projection of the domain on the half-way plane possess reflection symmetry through this origin. This reflection symmetry becomes unique to the half-way plane whenever the molecular axes are not perpendicular to the gas–liquid interface. This is the main characteristic of the half-way plane and is the reason for choosing to work in it rather than in the plane of the interface, for example.

For the special case of vertically oriented molecules any plane parallel to the gas–liquid interface also possess a similar reflection symmetry. Nevertheless, we will work in the half-way plane in order to simplify the junction between this paper and the following one dealing with inclined molecules. The cross sectional area of the molecules in the half-way plane will be designated by σ and is given by

$$\sigma = \frac{\sigma_0}{\cos \theta}. \tag{4}$$

In the case we consider here, the molecular axes are parallel to the domain axis. Thus $\sigma = \sigma_0$, see figure 2. The cross section of the domain in the half-way plane is designated by S, and is given by

$$S = \pi R^2. \tag{5}$$

The surface area occupied by the molecules in the half-way plane is designated by S_0 and is given by

$$S_0 = N\sigma. \tag{6}$$

2.2. The two dimensional model

Due to the cylindrical symmetry of the problem, the three dimensional close packing problem is equivalent to, and thus can be reduced to, a two dimensional problem (on the half-way plane) of close packing of circular discs of radius r_0 and surface area $\sigma = \sigma_0$, into a larger circular disc of radius R and surface area S as shown in figure 3. The discs of radius r_0 will be referred to as the "molecular disc" while the disc of radius R will be referred to as the "domain disc".

Let σ' be the average allocated area per molecular disc, therefore

$$\sigma' = \frac{S}{N}. \tag{7}$$

We define the "relative molecular area" Γ_m by

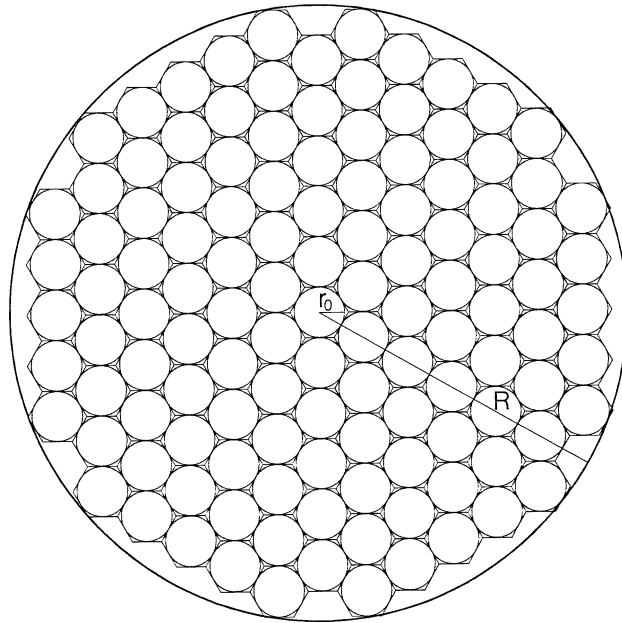$$\Gamma_m = \frac{\sigma'}{\sigma}. \tag{8}$$

Figure 3. Hexagonal close pack of spherocylindrical molecules: top view of rod-like molecules enclosed in a large circular cylindrical domain of radius R.

Combining equations (1)–(6) and (7), (8), and remembering that $\theta = 0$, we have

$$\Gamma_m = \frac{1}{N}\left(\frac{R}{r_0}\right)^2. \tag{9}$$

Let ρ' denote the "average number density" of molecular discs on the surface of the domain disc,

$$\rho' = \frac{1}{\sigma'}, \tag{10}$$

and define ρ as the number density of arbitrarily deformable close packed discs of constant area σ that occupy the whole surface S of the domain disc. That is,

$$\rho = \frac{1}{\sigma}. \tag{11}$$

It is also convenient to define the "relative number density" (or packing fraction) β by

$$\beta = \frac{\rho'}{\rho}. \tag{12}$$

Combining equations (9) and (10)–(12) we have

$$\beta = \frac{1}{\Gamma_m} = \frac{N}{(R/r_0)^2}. \tag{13}$$

The "relative loss of area" is given by

$$\delta_\sigma = \frac{S - S_0}{S_0} = \frac{\sigma' - \sigma}{\sigma} = \Gamma_m - 1 \qquad (14)$$

and the "relative loss of density" by

$$\delta_\rho = \frac{\rho' - \rho}{\rho} = 1 - \beta. \qquad (15)$$

The problem of close packing is that of minimizing δ_σ, δ_ρ or Γ_m, or equivalently of maximizing β. The absolute minimum values of δ_σ and δ_ρ are both zero while the absolute maximum value of β is unity.

2.3. The asymptotic limit $R/r_0 \rightarrow \infty$

It is helpful to start by briefly exposing the essential features of the very well understood asymptotic limit ($R/r_0 \rightarrow \infty$) of the problem; that is the case of close packing of circular discs on an infinite surface. This permits us to introduce, in familiar circumstances, the parameters and concepts that we will need later on. It will also permit us to separate the area loss due to hexagonal packing from area loss due to boundary effects.

Let the molecular discs be uniformly distributed over the "infinite" surface in some orderly fashion. To get a quantitative handle on the relative unoccupied area δ_σ we turn to the problem of tiling an infinite surface [4]. The collection of tiles that we use must cover the whole surface, and each tile must circumscribe one (and only one) disc. Remember that the circumference of a circular disc is a regular polygon with an infinite number of sides. Thus, for reasons of symmetry, it is evident that among all polygons having p sides with p fixed, and circumscribing the disc, the one having the smallest area is necessarily a regular polygon. The ratio $G(p)$ of the area of the regular polygon of p sides to that of the inscribe disc is given by [4]

$$G(p) = \frac{p}{\pi} \tan \frac{\pi}{p}. \qquad (16)$$

As can be easily verified, for $p \geqslant 3$, $G(p)$ is a decreasing function of p and goes asymptotically to 1 as $p \rightarrow \infty$. So the problem of minimizing δ_σ is reduced to the problem of finding the regular polygon with the largest number of sides that covers the surface. Only three regular polygons can tile an infinite surface: those having $p = 3$, 4 and 6 [4,8]. The corresponding values of $G(p)$ are: 1.66, 1.27 and 1.10. Consequently δ_σ is minimized by hexagonal tiling of the infinite surface. This is referred to as hexagonal packing of the discs. It is thus convenient to define

$$\gamma = G(6) = \frac{6}{\pi} \tan \frac{\pi}{6} = \frac{2\sqrt{3}}{\pi} = 1.1027. \qquad (17)$$

In this special case of tiling an infinite surface the relative molecular area (Γ_m), the relative density (β), the relative loss of area (δ_σ), and the relative loss of density (δ_ρ) have the following values:

$$\Gamma_m = \gamma = 1.1027, \tag{18}$$

$$\beta = \frac{1}{\gamma} = 0.9068, \tag{19}$$

$$\delta_\sigma = \gamma - 1 = 0.1027, \tag{20}$$

$$\delta_\rho = \frac{\gamma - 1}{\gamma} = 0.0931. \tag{21}$$

Combining equations (8) with (18) and (12) with (19) we have

$$\sigma' = \gamma\sigma, \tag{22}$$

$$\rho' = \rho\left(\frac{1}{\gamma}\right). \tag{23}$$

It is important to remember that the above equations (18)–(21), (22), (23) and accompanying numerical values are valid only for the limiting case $R/r_0 \to \infty$. So packing of discs on an infinite surface cannot be done with less than about 10% loss of area. Boundary effects in the packing of discs on a finite surface will induce additional loss of area.

2.4. R/r_0 finite

An hexagon can tile an infinite surface but it cannot tile a disc (figure 3). The non tillable portion near the perimeter of the disc produces an additional unoccupied area and increases the value of δ_σ. That is, the contribution of the boundary effect to the relative loss of area arises directly from the fact that a disc is not tillable. So there are four surface areas involved in the analysis: (i) the surface area of the domain disc $S = \pi R^2$; (ii) the surface area occupied by the molecular discs $S_0 = N\sigma$; (iii) the tillable surface area S_t; and (iv) the non tillable surface area of the domain disc S_n,

$$S_n = S - S_t. \tag{24}$$

It is worthwhile noting that $S_t \neq N\gamma\sigma$. To see this we turn to figure 3 and note that while all the molecular discs are wholly included in the domain disc, this is not true of the circumscribing hexagons. Consequently, the surface area covered by these hexagons is not, strictly speaking, part of the hexagonally tillable surface on the domain disc. Thus

$$S_t = (N - n)\gamma\sigma, \tag{25}$$

where n is the number of molecular discs inside the perimeter of the domain disc but whose circumscribing hexagons are not fully included inside the domain disk.

Following the same line of reasoning, the non-tillable surface S_n is not all empty lost space but does include the n molecular discs mentioned above. Hence S_n is made of two parts:

$$S_n = S_{n1} + S_{n2}, \tag{26}$$

where

$$S_{n1} = n\sigma, \tag{27}$$

which is the total sum of the areas occupied by molecular discs in the non tillable region, while S_{n2} is the total sum of the areas which are empty of both hexagons and molecular discs in the non tillable region.

Thus the relative loss of area per molecular disc is $(\gamma-1)$ for the $(N-n)$ molecular discs in S_t, and $((S_n/S_{n1}) - 1)$ for the n molecular discs in S_n. Consequently, the average relative loss of area per molecular disc due to hexagonal packing and boundary conditions combined is then given by the weighted average of these two relative losses:

$$\delta_\sigma = \frac{1}{N}\left\{(N - n)(\gamma - 1) + n\left[\frac{S_n}{S_{n1}} - 1\right]\right\}. \tag{28}$$

The above expression can also be formally derived using definition (14) for δ_σ. Furthermore, making use of equations (2), (4), (5), (14), (24), (25), (27) and (28), we recover equation (9) as expected.

In the remainder of this work hexagonal tilling will be used to establish an hexagonal reference lattice that will allow us to quantitatively formulate the conditions that guarantee that a molecule is fully inside the domain, and this is the only physically significant condition. The fact that the hexagons circumscribing the boundary molecular discs are partly outside the domain perimeter has no consequence and no physical significance. Nonetheless, in the previous paragraph, we analyzed the situation in detail to avoid all rash conclusions and pitfalls.

As we have seen thus far, the central parameter in determining the close packing of right circular cylindrical molecules in a right circular cylindrical domain is the relative molecular area Γ_m defined by equation (8). As can be seen from equation (9), Γ_m is given in terms of two parameters: N, the maximum number of molecules that can be packed in the domain, and R/r_0, the ratio of the domain radius to molecular radius. In order to obtain Γ_m in terms of one parameter only, we need to establish a relation between the above two parameters: that is N in terms of R/r_0. To achieve this we first need to introduce the geometry of the lattice defined by the centers of the hexagonally packed molecular discs.

3.   Geometry of the hexagonal lattice

3.1. *Hexagonal packing*

Consider the close packing of circular molecular cross-sections (molecular disc) of radius r_0 inside a larger disc (domain disc) of radius R (figure 3). As shown in the previous section this packing is optimal when the tiling (of the tillable portion S_T of the domain disc) is by regular hexagons. This tiling covers most of the surface of the domain disc but not all of it. The part not covered is near the circumference thus leading to boundary effects.

3.2. *System of axes*

Let the center of the domain disc (domain cross section in the half-way plane) coincide with the center of a molecular disc (molecular cross section in the half-way plane) and choose this common center as the origin of coordinates. Due to the hexagonal symmetry, there are six molecules that are nearest neighbors to the central molecule (figure 4). Their cross-sections are tangent to the central molecule and to each other. We draw three lines, each passing through the center of the central molecular disc and the centers of two of the six tangent neighbors. These axes are three axes
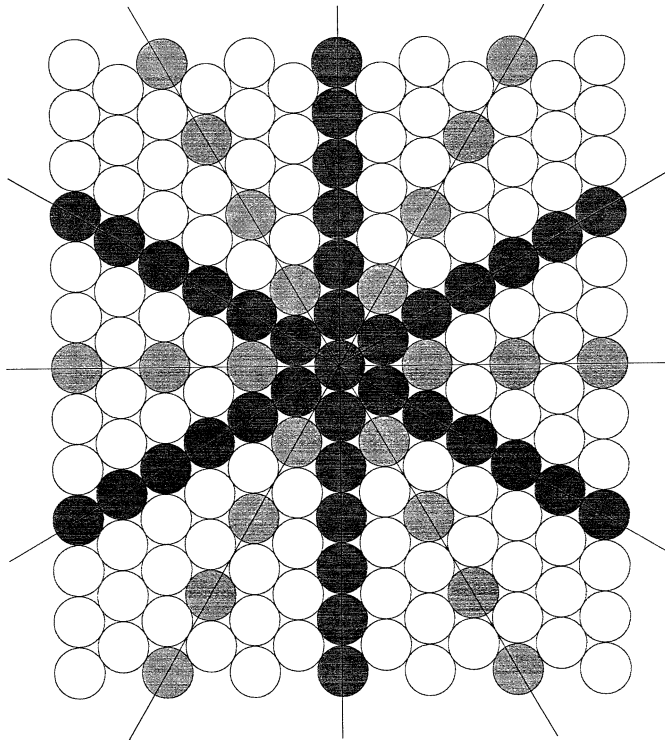

Figure 4. Axis of symmetry of an hexagonal packing in a non tilted situation.

of symmetry of the hexagonal close packing and are separated by 60°. They have the characteristic that the circular molecular discs of radius r_0 whose centers fall on these axes are successively tangent to each other (their centers are separated by a distance $2r_0$) as shown in figure 4. We designate these axes as the principal axis of symmetry and choose one of them as our Y axis. The X axis then bisects the angle between the other two principal axes of symmetry. Notice that the X axis is also an axis of symmetry, and is actually one of the three remaining axes of symmetry. We designate these as secondary axes of symmetry. The circular molecular disc whose centers fall on these three secondary axes are not successively tangent to each other. (Their centers are separated by a distance greater than $2r_0$.)

3.3. Lattice of the molecular centers

Let us inscribe the domain disc of radius R in a square whose sides are parallel to the X and Y axes, respectively. We will introduce a grid inside the square formed by lines parallel to the X and Y axes, respectively (figure 5). The intersections of the grid lines produces a lattice. By appropriately choosing the distance between the horizontal lines and vertical lines of the grid we can insure that the center of every molecular cross-section falls on the lattice.

In order for the center of the molecular disc to fall on a lattice site, the distance between horizontal lines must be equal to r_0 and the distance between vertical lines must be $\sqrt{3}r_0$ as shown on figure 5. Consequently, the radius vector from the origin
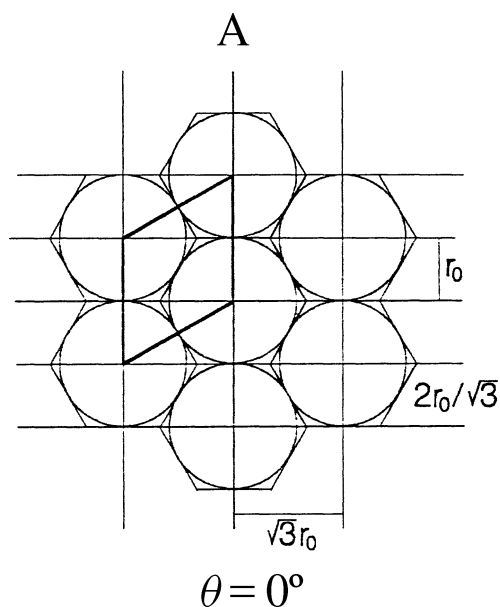

Figure 5. Primitive lattice cell of rod-like molecules in a non tilted situation.

to a lattice site is given by

$$\vec{r}_{lm} = r_0\big(\vec{i}\sqrt{3}l + \vec{j}m\big), \tag{29}$$

where l and m are integers. Notice that only half the lattice sites are occupied by molecules: actually the nearest neighbors to every occupied lattice site are empty, and the nearest neighbors to every empty latice site are occupied. It is thus seen that the lattice sites occupied by the centers of the molecular discs falling completely within the domain are given by the following conditions:

$$l + m = 2k, \tag{30}$$

where k is an integer, and

$$r_{lm} \leqslant R - r_0. \tag{31}$$

Equation (30) selects the lattice sites that are occupied by the centers of molecular discs, and equation (31) insures that the molecular discs are fully inside the domain disc. Combining equations (29) and (30) gives the distance from the origin to a lattice site containing the center of a molecular disc:

$$r_{lm} = 2r_0\sqrt{l^2 + k^2 - kl}, \tag{32}$$

where the integers k and l are not subject to any correlation condition. Furthermore, using equation (32), the condition given by equation (31) becomes

$$r_0\big(1 + 2\sqrt{l^2 + k^2 - kl}\big) \leqslant R. \tag{33}$$

Inequality (33) gives us the condition that l and k must satisfy in order for l and m to be, via equation (29), the coordinates of the center of a molecular disc which lies fully on the domain disc. It can be rewritten as

$$f_l(k) = k^2 - lk + l^2 - \left(\frac{R - r_0}{2r_0}\right)^2 \leqslant 0. \tag{34}$$

In order to minimize the boundary effects, the circle circumscribing the domain must be tangent to at least one molecular disc. By symmetry, it will also be tangent to at least five others. To realize this optimal condition, the equality in equation (34) must be satisfied for the coordinates of the above mentioned outermost molecules. Thus, not all values of R provide acceptable minimal radii for circumscribing the domain. Only those satisfying the equality in expression (33), for some value of the integer pair, l, k, are acceptable. Using non minimal radii artificially reduces the number density.

4. The number $N(R)$ of molecules in a domain of radius R

In this section we will evaluate the function $N(R)$, including boundary effects, for the case of vertically aligned molecules (figure 1 with $\theta = 0$). N is the number of molecules in the domain and R is the radius of the base of the domain (figure 3). In

order to evaluate the function $N(R)$, we note that for every pair of integers, l and k satisfying inequality (34), we have a molecule inside the domain. Expression (34) is a quadratic inequality in k and since the coefficient of k^2 is positive, the inequality is satisfied in between the roots ($k_{\min}$ and $k_{\max}$) of the equation $f_l(k) = 0$. Thus, only the integer values of k satisfying $k_{\min} \leqslant k \leqslant k_{\max}$ identify a molecule inside the domain, that is,

$$\left[\frac{l - \sqrt{\Delta}}{2}\right]^+ \leqslant k \leqslant \left[\frac{l + \sqrt{\Delta}}{2}\right]^-, \tag{35}$$

where $[x]^+$ indicates the smallest integer greater than or equal to x, $[x]^-$ indicates the largest integer smaller than or equal to x, and

$$\Delta = \left(\frac{R}{r_0} - 1\right)^2 - 3l^2. \tag{36}$$

The positivity of Δ is the only restriction on the allowable integer values of l. The number of allowable k values for every allowed value of l is

$$N_k(l) = \left[k_{\max}\right]^- - \left[k_{\min}\right]^+ + 1 = \left[\frac{l + \sqrt{\Delta}}{2}\right]^- - \left[\frac{l - \sqrt{\Delta}}{2}\right]^+ + 1. \tag{37}$$

To evaluate this expression we have to consider the case, where l is even, and the case, where l is odd, separately. We also need to make use of the fact that, for an integer q, $[q]^+ = [q]^- = q$. Furthermore, $[-x]^+ = -[x]^-$ and, similarly, $[-x]^- = -[x]^+$. First, let $l = 2q$ be even, then

$$N_k(2q) = q + \left[\frac{\sqrt{\Delta}}{2}\right]^- - q + \left[\frac{\sqrt{\Delta}}{2}\right]^- + 1, \tag{38}$$

$$N_k(2q) = 2\left[\frac{\sqrt{(R/r_0 - 1)^2 - 3(2q)^2}}{2}\right]^- + 1. \tag{39}$$

Next, let $l = 2q - 1$ be odd, then

$$N_k(2q - 1) = q - 1 + \left[\frac{1 + \sqrt{\Delta}}{2}\right]^- - q + \left[\frac{1 + \sqrt{\Delta}}{2}\right]^- + 1, \tag{40}$$

$$N_k(2q - 1) = 2\left[\frac{1 + \sqrt{(R/r_0 - 1)^2 - 3(2q - 1)^2}}{2}\right]^-. \tag{41}$$

All constraints having been satisfied, the only requirement on the value of l is that the above square roots appearing in equations (39) (for l even) and (41) (for l odd) be real. Hence,

$$-\left[\frac{(R/r_0 - 1)}{\sqrt{3}}\right]^- = -p \leqslant l \leqslant p = \left[\frac{(R/r_0 - 1)}{\sqrt{3}}\right]^-. \tag{42}$$

Consequently, the number $N(R)$ of molecules in a domain of radius R is given by

$$N(R) = \sum_{l=-p}^{p} N_k(l). \tag{43}$$

At this stage, we have two options to evaluate $N(R)$. We can evaluate the sum in equation (43) to obtain an exact expression for $N(R)$, but this expression will not be in closed form, or alternatively, we can approximate the sum in equation (43) by an integral and obtain an approximate, but closed form, expression for $N(R)$ which is valid for $R/r_0 \gg 1$. We will do both.

4.1. Exact non closed expression for $N(R)$

Since the Y axis is an axis of symmetry, then $N_k(-l) = N_k(l)$, as is evident from equations (39) and (40). Hence equation (43) can be rewritten as

$$N(R) = N_k(0) + 2 \sum_{l=1}^{p} N_k(l) \quad \text{for } p \geqslant 1. \tag{44}$$

Since the functional form of $N_k(l)$ depends on whether l is even or odd, the sum in equation (44) is separated into even and odd parts:

$$N(R) = N_k(0) + 2(1 - \delta_{p0} - \delta_{p1}) \sum_{q=1}^{[p/2]^-} N_k(2q) + 2(1 - \delta_{p0}) \sum_{q=1}^{[(p+1)/2]^-} N_k(2q-1), \tag{45}$$

where δ_{ij} is the Kronecker delta. Introducing equations (39) and (41) for $N_k(2q)$ and $N_k(2q-1)$ gives

$$N(R) = N_k(0) + (1 - \delta_{p0} - \delta_{p1})\big(4\xi_2 + 2\xi_2'\big) + (1 - \delta_{p0})4\xi_1, \tag{46}$$

where

$$\xi_1 = \sum_{q=1}^{[(p+1)/2]^-} \left[\frac{1 + \sqrt{(R/r_0 - 1)^2 - 3(2q-1)^2}}{2} \right]^-, \tag{47}$$

$$\xi_2 = \sum_{q=1}^{[p/2]^-} \left[\frac{\sqrt{(R/r_0 - 1)^2 - 12q^2}}{2} \right]^- \tag{48}$$

and

$$\xi_2' = \sum_{q=1}^{[p/2]^-} 1 = \left[\frac{p}{2} \right]^-. \tag{49}$$

Equations (46)–(49) give a complete and exact solution to the problem. Given R and r_0, p can be evaluated by equation (42). ξ_1, ξ_2, and ξ_2' can then be evaluated by equations (47)–(49). This, in turn, will lead to N as a function of R via equation (46).

4.2. Approximate closed expression for N

For large values of R/r_0, we can approximate the summation in equation (43) by an integration. To be able to integrate, the integrand must be at least a piecewise continuous function. On the other hand, the integrand $N_k(l)$, as given by equation (37), is not a piecewise continuous function of l. To approximate $N_k(l)$ by a continuous function, we note that $x - 1 < [x]^- \leqslant x$. It is thus reasonable to approximate the value of $[x]^-$ by its average value $x - 1/2$. This way, in going over from a discrete to a continuous function, we avoid largely overestimating or largely underestimating the value of the function. Similarly, $x \leqslant [x]^+ < x + 1$ and thus $[x]^+$ can be approximated by $x + 1/2$. As for the limits of integration, we simply approximate p as given in equation (42) by the term $(R/r_0 - 1)/\sqrt{3}$. Combining the above operations, we obtain the following integral expression for $N(R)$:

$$N(R) \approx \sqrt{3} \int_{-(R-r_0)/(\sqrt{3}r_0)}^{(R-r_0)/(\sqrt{3}r_0)} \mathrm{d}x \sqrt{\left(\frac{R-r_0}{\sqrt{3}r_0}\right)^2 - x^2}. \tag{50}$$

As x goes from the lower to the upper limit of integration, the integrand

$$y(x) = \sqrt{\left(\frac{R-r_0}{r_0\sqrt{3}}\right)^2 - x^2} \tag{51}$$

describes a semi-circle of radius $(R - r_0)/(r_0\sqrt{3})$. Evaluating the integral we obtain

$$N(R) \approx \frac{1}{\gamma}\left(\frac{R-r_0}{r_0}\right)^2 \quad \text{for } \frac{R}{r_0} \gg 1. \tag{52}$$

Inverting equation (52) we obtain the value of the radius R of the right circular cylinder inscribing the N close packed molecules of the domain as

$$R \approx r_0\left(\sqrt{\gamma N} + 1\right). \tag{53}$$

5. The average density

Combining equations (5), (7) and (10), we obtain

$$\rho' = \frac{N}{\pi R^2}; \tag{54}$$

this result is also evident from the definition of ρ'. To obtain the exact value of ρ' we use the value of N as given in equation (46). For large values of N we can use the approximate expression (52) to obtain

$$\rho' \approx \rho\left(\frac{1}{\gamma}\right)\left(\frac{R-r_0}{R}\right)^2. \tag{55}$$

Combining equations (53) and (55) we obtain the average surface density in terms of the number of molecules in a domain

$$\rho' \approx \rho\left(\frac{1}{\gamma}\right)\left(1 - \frac{2}{\sqrt{\gamma N} + 1}\right)^2.$$

(56)

The first term in equations (55), (56), ρ, is the density of deformable molecular discs that can fill the whole surface; the second term, $1/\gamma$, is the hexagonal packing correction for "rigid" molecular discs; and the third term is the correction due to boundary effects. The relative number density β is defined by equation (12) and is given in terms of N and R/r_0 by equation (13). To obtain the exact value of β we use the value of N as given by equation (46). On the other hand for large value of N we have, through equations (12) and (55),

$$\beta = \frac{1}{\gamma}\left(1 - \frac{r_0}{R}\right)^2.$$

(57)

6. Results and discussion

6.1. The plots

The comparison between the exact and approximate form of β as a function of R/r_0 is given in figure 6. In this figure, the solid line (—) is the plot of the approximate form of β as a function of R/r_0 obtained from equation (57) while the dots ($\cdots$) are the exact form. As discussed in section 3.3, the latter is calculated by avoiding non minimal radii R that would artificially reduce the number density, and thereafter artificially reduce the value of β. To achieve this, the values of R are calculated from the pair of integers (l, k) by requiring that the equality sign holds in expression (33). From the resulting equation (33) it is evident that for any couple (l, k), the radius R obtained is the same as that obtained from the couple $(-l, -k)$ or from the couple $(l, l - k)$. By increasing l, starting from 1 and varying (k) from 0 to $[l/2]^-$, one is assured that all the resulting values of R satisfy the condition of minimal radius. The successive values of R produced by this method of calculation are non monotonic. Once R is chosen as a minimal radius, the value of β is determined by expression (13) with equation (46).

6.2. Comparison between exact and approximate values of β

Figure 6 indicates that for large values of R/r_0, the approximate expression (57) is precise enough to simplify the calculations of β. For a precision level of 1%, expression (57) can be used for values of R such that $R/r_0 \geqslant 100$, that is, for domains containing more than about 10 000 molecules per domain. For such a domain the total relative area loss is around 13%: 10.3% coming from the hexagonal packing and around 2.5% from the boundary effects. An $R/r_0 = 100$ corresponds, for example, in
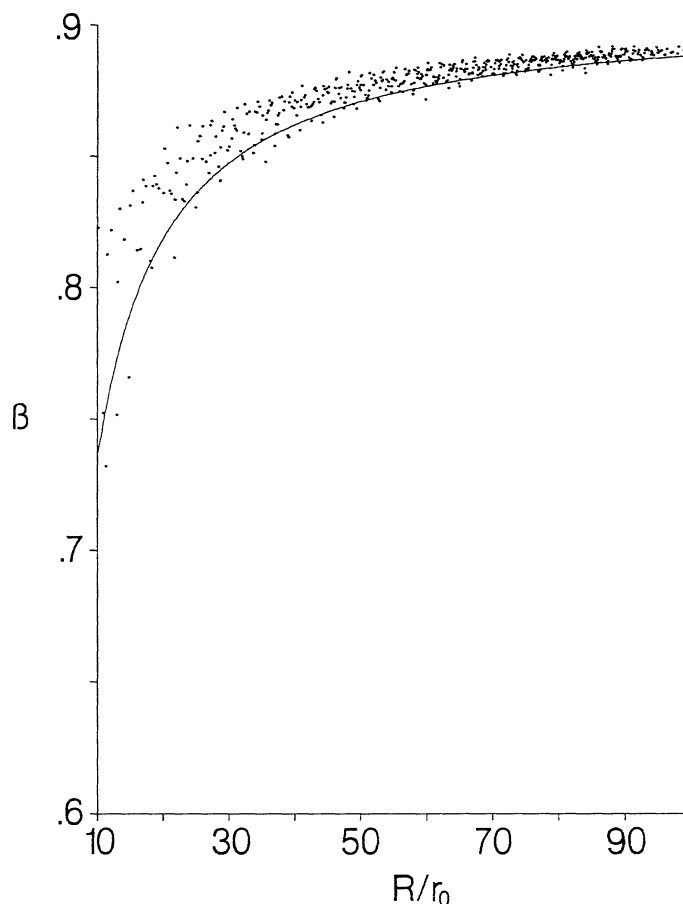
Figure 6. Number density functions, β, as a function of the relative size of the domain R/r_0. The solid line (—) is the plot of the approximate form while the dots ($\cdots$) represent the exact form.

the case of a simple chain lipidic molecules with a radius $r_0 = 2.25$ Å to a domain with a diameter ($2R$) of 450 Å.

Kjaer et al. [10] have reported a correlation length of 150 Å for monolayers of arachidic acid on the surfaces of pure water and salt solutions using synchrotron X-ray diffraction measurements. This indicates that domains, where local molecular organization is coherent, have a diameter $2R$ of approximately 150 Å. Since for single-chained lipidic molecules $r_0 = 2.25$ Å, then, with molecules vertically aligned (as reported) the value of R/r_0 is 33. From figure 6 we find that boundary effects give a total relative loss of 17.1%: 10.3% from the hexagonal packing and 6.8% from the boundary effects. The latter loss is 66% of the surface area loss due to the close pack organization.

Dutta et al. [6], using X-ray diffraction measurements on lead stearate and ligno-ceric acid films on water reported a correlation length of about 250 Å. The difference between the average molecular area they obtained from pressure-area measurements

on the through ($\sim$19 Å^2) and the local molecular area obtained from the X-ray lattice measurements (17.8 Å^2) is around 6.7% [6]. The value of the correlation length gives the diameter ($2R$) of the average domain. Thus with an $r_0 = 2.25$ Å and with the molecules vertically aligned, as reported, the value of R/r_0 is 56. From figure 6 we evaluate the total relative surface area loss to be 14.1%: 10.3% from the hexagonal close packing and 3.8% from the boundary effects. Our calculations give the absolute minimum surface area loss due to boundary conditions resulting from geometrical factors exclusively. Our predictions of this absolute minimum for the systems of Dutta et al. [6] mentioned above is 3.8%. This is consistent with the measured effect of around 6.7%.

7.   Conclusion

The relative molecular area Γ_m gives the ratio of the average molecular area obtained from the case of close packing of "rigid" molecules to the molecular area obtained for the case of "deformable" molecules. It is of course the rigidity of the molecules that produces a difference between molecular area and average molecular area. "Deformable" molecules would, of course, fill the whole domain leaving no empty space.

From the results of our analysis we conclude that the boundary effects are a non negligible factor in the packing of molecules on a liquid surface and should be taken into consideration whenever we use density measurements to deduce molecular parameters and this even in the simple case studied here of non tilted spherocylindrical molecules. For the case of tilted molecules the boundary effects are even greater. As expected, the relative importance of boundary effects increases with decreasing domain size. Consequently, the present calculation allows us to determine the minimum size of a domain for which boundary effects can be neglected.

We have established the organizational "background" structure that should be expected under rather general conditions for molecules grouped in domains at the interface. Deviations arising from the specific configuration of the molecules are thus highlighted and can then be studied as perturbations superimposed on this primitive structure.

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