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

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We derive an upper limit, imposed by cinematic constraints, for the packing fraction of right circular spherocylindrical molecules inside a freely rotating right circular cylindrical domain at a gas–liquid interface. The derivation is made under the assumption that the molecules are rigid and close packed. The expression obtained for the packing fraction as a function of domain size and angle of inclination is exact for all domain sizes and all values of the inclination angle. For small angles of inclination ($\theta \leqslant 20°$) and domains containing more than 30 molecules, the packing fraction can be approximated by a simple smooth analytical expression. The domain size at which the approximation is reasonable increases with increasing angle of inclination. At $\theta = 40°$ the approximation is good for domains containing 300 molecules or more.

1. Introduction

In this paper as in [7] we are concerned with the molecular organization of Langmuir films at the liquid–gas interface. Specifically we study the close packing of homogeneous right circular spherocylindrical molecules (figure 1) inside a right circular cylindrical domain whose axis is perpendicular to the interface. In [7] we studied the case where the molecular axes were aligned perpendicular to the interface. In the present paper we consider the more general case of inclined molecules. We will evaluate the average density inside the domain as a function of the size of the domain and of the inclination of the molecules to the interface. For this purpose we need to evaluate the number $N(R, \theta)$ of close packed molecules in the domain as a function of the domain radius R and the molecular inclination angle θ. The molecular radius r_0 serves as the unite of distance and establishes the scale.

The problem of packing vertically aligned molecules is easily reducible to a two-dimensional tiling problem [7]. On the other hand, the problem of packing inclined
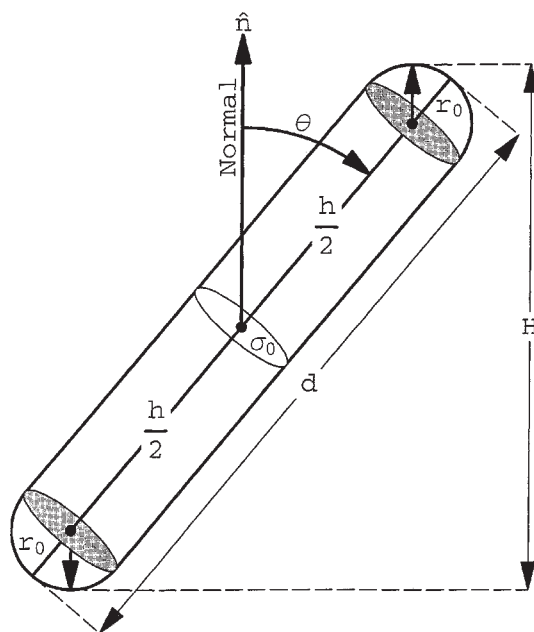
Figure 1. Parameters of the spherocylindrical rod-like model of a molecule. The vector $\hat{n}$ is normal to the liquid–gas interface.

molecules is inherently three-dimensional, and its reduction to a two-dimensional tiling problem requires the use of projective geometry.

In the case of vertically aligned molecules the relative loss of area (deviation of the packing fraction from its maximum value of unity) is due to two factors: (1) the expected loss of area due to hexagonal packing and (2) the additional loss of area due to the breakdown of hexagonal packing near the boundary of the circle. On the other hand, in the case of inclined molecules, the loss of area is determined by four factors: (i) the inclination of the peripheral molecules (which increases the volume of the domain cylinder); (ii) the hydrophobically driven vertical realignment of the molecules (which stretches the lattice in the half-way plane); (iii) the horizontal reorganization of the molecules (which minimizes the volume of the domain cylinder subject to the constraints of inclination and hydrophobicity); and (iv) the breakdown of the hexagonal tilling near the boundaries.

In this paper we will examine these factors and quantitatively evaluate their collective contribution to the packing fraction of rod-like spherocylindrical molecules inside a right circular cylindrical domain.

2.   The model

As in [7], the mathematical problem at hand is that of close packing of parallely oriented right circular spherocylindrical (rod-like) molecules into a larger cylindrical

(barrel-like) domain. But while in [7] we considered the special case where the molecular axes are parallel to the domain axis (perpendicular to the interface), in the present work we relax this condition and consider the more general case where the molecular axes make an angle θ with the normal to the interface. That is, the molecular axes are inclined at an angle θ relative to the domain axis. We will only present the essential elements of the model and refer the reader to [7] for further details.

2.1. The molecules

The molecules are spherocylinders [1] 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

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

and its cross-sectional area σ_0, which we refer to as the molecular disc, is

$$\sigma_0 = \pi r_0^2. \tag{1b}$$

2.2. 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. The N molecules are collectively inclined at an angle θ to the vertical (the normal to the gas–liquid interface), as shown in figures 2 and 3. We refer to this group of N parallel molecules as the "physical domain". The spherical polar heads are tangent to a plane parallel to the interface. Due to the dimensions of the single chain lipid molecules and the number of molecules in a domain, these physical domains are generally rather flat.

The "circumscribing domain" or simply the domain is modeled as a right circular cylinder enveloping the N molecules of the "physical domain". The axis of this cylinder is 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. Thus the height H of the cylinder is determined by the inclination of the molecules relative to the interface:

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

As for the radius R, it is equal to half the largest dimension of the projection of the "physical domain" on the interface.

2.3. 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 (figures 2 and 3). The cross-section of the domain in the half-way plane is a disc of radius R. The symmetry axis of the domain passes through the center of this disc. This is the point that we
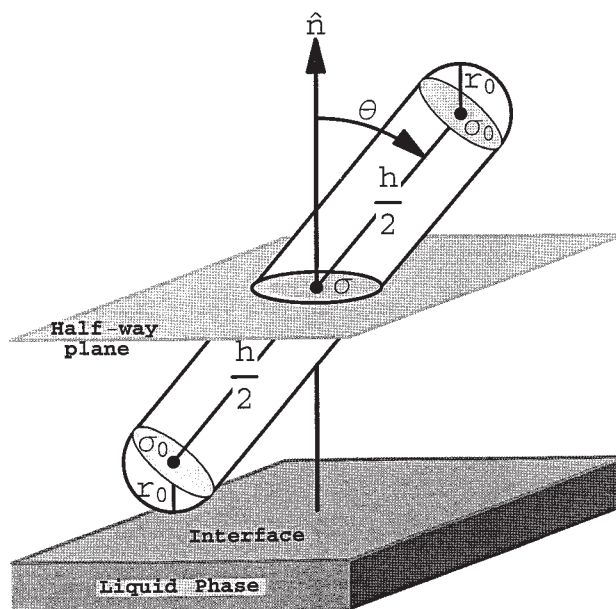
Figure 2. Spherocylindrical molecule at the liquid–gas interface. The half-way plane is parallel to the interface and passes through the center of symmetry of the molecule. The molecule is tilted by an angle θ with respect to the normal to the interface.

will take as the origin of the coordinates. The projection of the physical domain on the half-way plane possesses reflection symmetry through this origin. This reflection symmetry is unique to the half-way plane. 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.

The cross-sections of the spherocylindrical molecules in the half-way plane are elliptical discs of minor axis r_0 and major axis $r_0/\cos\theta$. The molecular axes pass through the centers of these ellipses. These centers define a lattice. Each ellipse is symmetrically centered in the middle of the projection of the corresponding molecule on the half-way plane. We introduce the following definitions in the half-way plane:

S the cross-section of the domain,
S_0 the total surface area occupied by the molecules,
σ the cross-sectional area of a molecule,
σ' the average allocated area per molecule,
Γ the relative molecular area,
ρ the number density of arbitrarily deformable close packed discs of constant area σ,
ρ' the average number density of molecular discs on the surface of the domain disc,
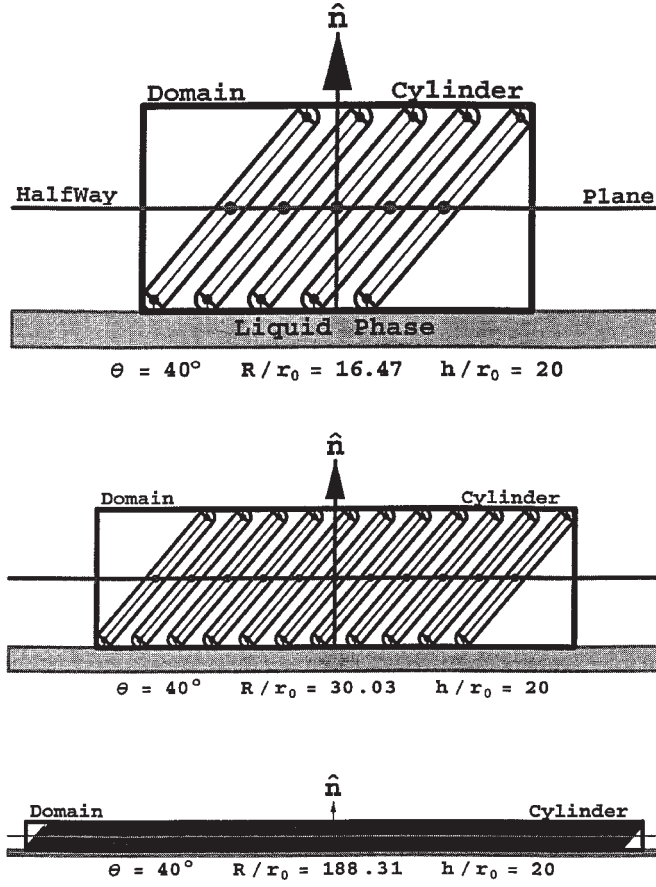β the packing fraction (or relative number density);

Figure 3. Domain cross-section in the inclining plane. The inclining plane is determined by the axis of the domain and a secondary axis of symmetry in the half-way plane. For the domains shown, the number of molecules whose axis lies in the inclining plane is 5, 11 and 81, respectively. For large domains, the domain is essentially a thin disc.

$$S = \pi R^2, \tag{3a}$$

$$S_0 = N\sigma, \tag{3b}$$

$$\sigma = \frac{\sigma_0}{\cos\theta}, \tag{3c}$$

$$\sigma' = \frac{S}{N} = \left(\frac{S}{S_0}\right)\sigma, \tag{3d}$$

$$\Gamma = \frac{\sigma'}{\sigma} = \frac{S}{S_0} = \frac{1}{N}\left(\frac{S}{\sigma}\right) = \frac{1}{N}\left(\frac{R}{r_0}\right)^2 \cos\theta, \tag{3e}$$

$$\rho = \frac{1}{\sigma}, \tag{3f}$$

$$\rho' = \frac{1}{\sigma'}, \tag{3g}$$

$$\beta = \frac{\rho'}{\rho} = \frac{\sigma}{\sigma'} = \frac{1}{\Gamma} = \frac{N\sigma}{S} = \frac{N}{\cos\theta}\left(\frac{r_0}{R}\right)^2. \tag{3h}$$

The problem of close packing is that of minimizing Γ, or, equivalently, of maximizing β. The absolute maximum value of β is unity.

3. The lattice

3.1. The reference lattice

The high degree of symmetry in the case of vertically oriented molecules simplifies the process of introducing and defining the system of axes as well as establishing the geometry of the optimal packing. As shown in [7], for the case of vertically oriented molecules, the optimal packing of rod-like molecules in a cylindrical domain is hexagonal (figure 4). The intersection of the molecular axes with the half-way plane produces a lattice with three principal and three secondary axes of symmetry. We introduce a system of axes as follows: (i) the z-axis coincides with the axis of the domain cylinder, that is with the normal to the interface; (ii) the intersection of the z-axis with the half-way plane defines the origin of coordinates; (iii) the xy-plane coincides with the half-way plane; (iv) the x-axis coincides with one of the secondary axes of symmetry; (v) the y-axis coincides with one of the principal axes of symmetry. Due to the hexagonal symmetry of the lattice, the above system of coordinates is orthogonal.

Relative to the above system of axes, the intersection of the molecular axes with the half-way plane produces, as shown in [7], a lattice whose sites are given by

$$\vec{r} = r_0\big(\hat{i}l\sqrt{3} + \hat{j}m\big), \tag{4a}$$

where l and m are integers. Only half the lattice sites defined by equation (4a) can potentially be occupied by molecules; the nearest neighbor to every occupied lattice site being necessarily empty (see [7]). For a lattice site to be occupied by the center of a molecular disc two more conditions need to be satisfied:

$$l + m = 2k, \tag{4b}$$

where k is an integer, and

$$r \leqslant R - r_0. \tag{4c}$$

Combining equations (4a) and (4b) we can rewrite the radius vector to a lattice site as

$$\vec{r}_{lk}(0) = r_0\big[\hat{i}l\sqrt{3} + \hat{j}(2k - l)\big], \tag{5a}$$

where l and k are now unconstrained integers. The zero in the argument of r_{lk} indicates that the above lattice corresponds to the case $\theta = 0$, that is, to the case of vertically
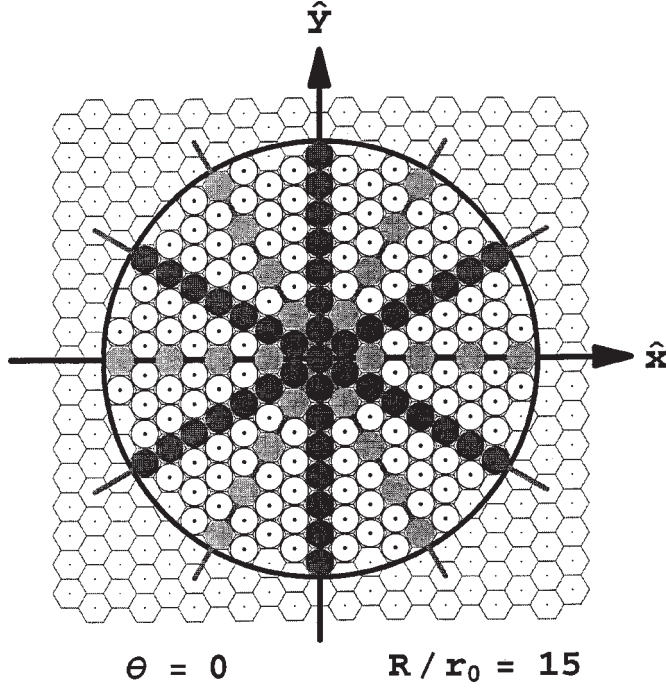
Figure 4. The hexagonal lattice (in the half-way plane) corresponding to vertically oriented molecules ($\theta = 0$). This is the "reference lattice" and is used to establish the reference coordinate system. The x- and y-axes coincide, respectively, with a secondary and a principal axis of symmetry. The origin lies on the intersection of the domain cylinder axis with the half-way plane.

aligned molecules. The distance from the origin to the center of a molecular disc on the half-way plane (the center of the cross-section of a molecule on the half way-plane) is thus given by

$$r_{lk}(0) = 2r_0 \sqrt{l^2 - kl + k^2}, \tag{5b}$$

subject to constraint (4c) as applied to r_{lk}. That is,

$$r_{lk}(0) \leqslant R - r_0. \tag{5c}$$

3.2. Lattice of the inclined molecules

The optimal tiling of the domain disc (cross-section of the cylindrical domain in the half-way plane) in the case $\theta = 0$ is, as shown in [7], by regular hexagons with the circumference of the molecular discs (cross-section of the molecules in the half-way plane) as inscribed circles. That is, the spherocylindrical molecules standing vertically are inscribed in right regular hexagonal cylinders ([7], figure 2). For convenience we take these "virtual" hexagonal cylinders to be infinite in length, thus allowing the inscribed spherocylindrical molecules to slide inside them. When the molecules in the domain are tilted at an angle θ to the vertical, the circumscribing hexagonal

cylinders are tilted with them at the same angle. As the tilting proceeds, the molecules continuously slid in the hexagonal cylinders in order to stay anchored to the base of the domain (to the gas–liquid interface).

The sensitivity of the results to the direction of inclination is relatively small, and this problem goes beyond the scope of the present paper. The small corrections involved will be dealt with subsequently. Mathematically it is easiest to deal with the case where the axes of the molecules are tilted in the xz-plane (or planes parallel to it), by an angle θ with respect to the z-axis. In this case the projections of the molecular axes on the half-way plane are all parallel to the x-axis, and further more the y- and x-axes retain their quality of principal and secondary axes of symmetry, respectively. Their in lies the main simplification.

The cross-sections of the spherocylindrical molecules in the half-way plane are elliptical. The minor axis of the ellipses is parallel to the axis of rotation (the y-axis), and the major axis of the ellipses is parallel to the plane of inclination (the xz-plane). The centers of the ellipses define a lattice in the half-way plane as shown in figure 5. The distance between the lattice grid lines which are parallel to the rotation axis (the y-axis) remains unchanged during the process of tilting, while the distance between the lattice grid lines parallel to the x-axis are stretched by a factor of $1/\cos\theta$. Hence, making use of equation (5a) we find that the lattice (in the half-way plane) of the centers of the inclined molecules is given by

$$\vec{r}_{lk}(\theta) = r_0 \left[\hat{i} \frac{l\sqrt{3}}{\cos\theta} + \hat{j}(2k - l) \right], \tag{6a}$$

where l and k are unconstrained integers. Equation (6a) gives the lattice sites through which a molecular axis can (on purely geometric grounds) potentially pass, but it does not guarantee that the corresponding molecule is inside the cylindrical domain. The length of the above vector is

$$r_{lk}(\theta) = 2r_0 \sqrt{\frac{1}{4}\left(1 + \frac{3}{\cos^2\theta}\right)l^2 - kl + k^2}. \tag{6b}$$

3.3. The inclusion problem

The equivalent of equation (5c), which guarantees that a potentially possible site is actually occupied, is more complicated to derive in the $\theta \neq 0$ case. If a site, satisfying equation (6a), is actually occupied by the center of an (elliptical) molecular disc, this means that the corresponding molecule is in the cylindrical domain, and consequently that the projection of this molecule in the half-way plane is fully included inside the circle of radius R circumscribing the (circular) domain disc. The projection of a molecule on the half-way plane is a rectangle of length $h\sin\theta$ bounded by two semi-circles of radius r_0 one at each end as shown in figure 6. The elliptical cross-section of a molecule in the half-way plane is symmetrically centered with respect to the projection of the molecule on this plane. To derive the equivalent of condition (5c)
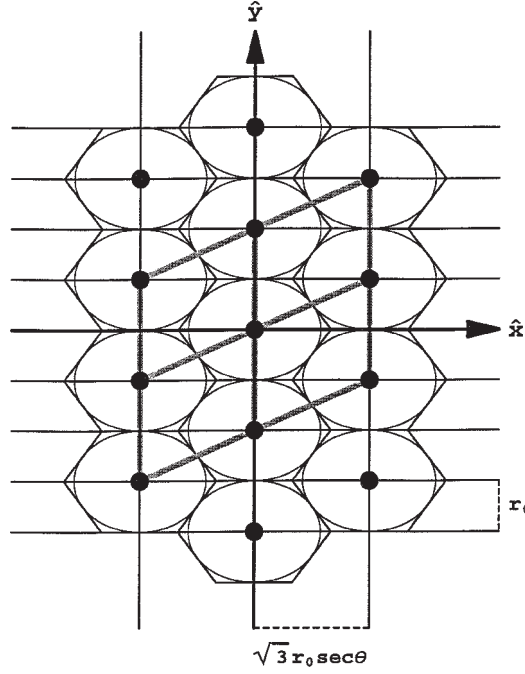
Figure 5. Lattice of inclined molecules. The elementary cells are parallelograms. Only half of the Cartesian lattice points are filled. The nearest neighbors to every filled site are empty and vice versa.

we need to determine the point of the molecular projection which is furthest from the origin. To determine this point we first need to parametrize this molecular projection.

3.3.1. Parameterizing the projection

We divide the projection of the molecule on the half-way plane into four segments (figure 6): two straight lines h_1 and h_3, and two semi-circles h_2 and h_4. The segments h_i and h_{i+1} have only one point in common which we label ν_{i+1}. That is, $\nu_{i+1} = h_i \cap h_{i+1}$, where the operation of addition in the subscript is to be understood as modulo 4.

The center of symmetry of the molecular projection on the half-way plane is designated by c and situated at a lattice site. The centers of the two end caps (semi-discs) are designated by c_1 and c_2. The vector from the origin of coordinates to c is $\vec{r}(l, k, \theta) = \vec{r}_{lk}(\theta)$ as given by equation (6a). The vectors from the origin of coordinates to c_1 and c_2 are respectively designated by $\vec{r}_1 \equiv \vec{r}_1(l, k, \theta)$ and $\vec{r}_2 \equiv \vec{r}_2(l, k, \theta)$, as shown in figure 6. When the context is unambiguous we will omit the functional dependence and simply write $\vec{r}_1$ and $\vec{r}_2$. These vectors are given by

$$\vec{r}_n(l, k, \theta) = \vec{r}(l, k, \theta) + (-1)^n \frac{h \sin \theta}{2} \hat{i}$$

$$= r_0 \left\{ \hat{i} \left[\frac{l\sqrt{3}}{\cos \theta} + (-1)^n \frac{h \sin \theta}{2r_0} \right] + \hat{j}(2k - l) \right\}, \quad n = 1, 2, \qquad (7a)$$

**PROJECTION OF A MOLECULE
ON THE HALF WAY PLAN**

THE FURTHEST POINT

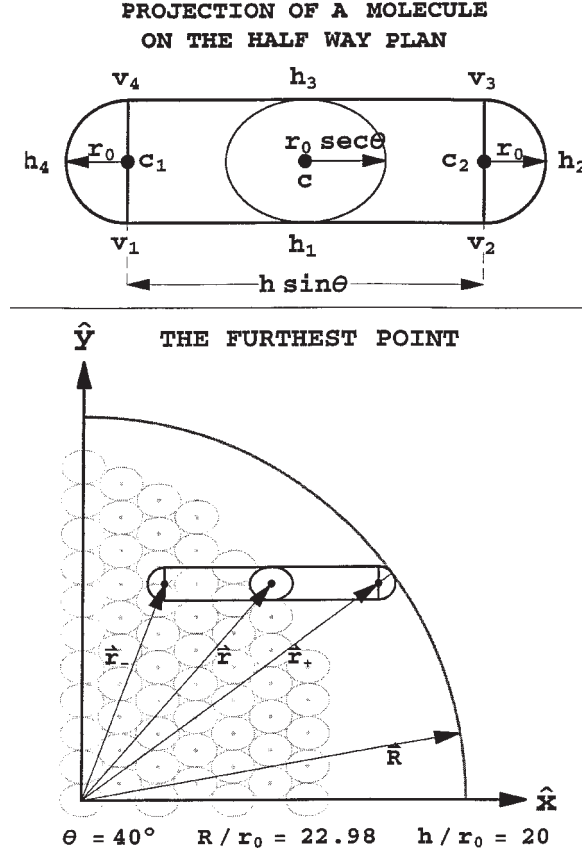$\theta = 40°$ $R/r_0 = 22.98$ $h/r_0 = 20$

Figure 6. Parameters of the projection of a molecule on the half-way plane. These parameters are needed in determining the furthest point of the molecular projection. This "furthest point" is, in turn, needed to determine the boundaries of the cross-section of the physical domain.

and their magnitudes are given by

$$r_n(l, k, \theta) = r_0 \sqrt{\frac{3l^2}{\cos^2 \theta} + \frac{h^2 \sin^2 \theta}{4r_0^2} + (2k - l)^2 + (-1)^n \frac{hl\sqrt{3}\tan\theta}{r_0}}, \quad n = 1, 2.$$

(7b)

The larger of the above two vectors will be designated by $\vec{r}_+$ and the smaller by $\vec{r}_-$. Since $\tan\theta \geqslant 0$ for $0 \leqslant \theta \leqslant \pi/2$ (which is the possible range of variation of θ), then

$$r_\pm(l, k, \theta) = r_0 \sqrt{\frac{3l^2}{\cos^2 \theta} + \frac{h^2 \sin^2 \theta}{4r_0^2} + (2k - l)^2 \pm \frac{h|l|\sqrt{3}\tan\theta}{r_0}},$$

(8a)

and this can be rewritten as

$$r_\pm(l, k, \theta) = 2r_0 \sqrt{\frac{1}{4}\left(1 + \frac{3}{\cos^2\theta}\right)l^2 - lk + k^2 + \left(\frac{h}{4r_0}\right)^2 \sin^2\theta \pm \left(\frac{h|l|\sqrt{3}}{4r_0}\right)\tan\theta}.$$

(8b)

The vector from c_i to the circumference of the corresponding semi-circle is designated by $\vec{r}_i'$. Its magnitude is $r_i' = r_0$. The vector from the origin of coordinates to the circumference of the semi-circle centered at c_i is designated by $\vec{r}_i''$. The vectors $\vec{r}_i$, $\vec{r}_i'$ and $\vec{r}_i''$ are related by

$$\vec{r}_i'' = \vec{r}_i + \vec{r}_i'.$$

(9)

Finally, we let $\vec{r}_p = (x_p, y_p)$, with components $x_p \equiv x_p(l, k, \theta)$ and $y_p \equiv y_p(l, k, \theta)$, be the radius vector from the origin of coordinates to a point P on the perimeter of the projection (in the half-way plane) of the molecule associated with the lattice site whose radius vector is $\vec{r}(l, k, \theta)$.

3.3.2. The furthest point

For all points on section h_1, y_p is constant. Consequently, the point of h_1 which is furthest from the origin is that having the largest absolute value of x_p, that is either ν_1 or ν_2 depending on the position of the molecule with respect to the y-axis. Similarly, the point on h_3 which is furthest from the origin is either ν_3 or ν_4. But these four vertices $(\nu_1, \nu_2, \nu_3, \nu_4)$ also lie on one or the other of the two semi-circles h_2 and h_4. Consequently, the point of the perimeter which is furthest from the origin must lie on one or the other of these two semi-circles, that is, it is given either by $\vec{r}_1''$ or by $\vec{r}_2''$. Hence the point of the molecular projection that is furthest from the origin is given by the maximum value of $\vec{r}_1''$ or the maximum value of $\vec{r}_2''$, which ever is greater. But $\vec{r}_i''$ is maximum when $\vec{r}_i$ and $\vec{r}_i'$ are parallel, as easily seen from equation (9). Hence,

$$\max(r_i'') = r_i + r_i' = r_i + r_0,$$

(10a)

and, consequently, the distance of any point on the periphery of the projection of the molecule on the half-way plane satisfies the inequality

$$r_p \leqslant \text{larger of } \{\max(r_1''), \max(r_2'')\} = r_+ + r_0.$$

(10b)

3.3.3. The constraint

For a molecule to be fully contained in the cylindrical domain, its projection on the half-way plane must be fully contained inside the domain disc (cross-section of the domain cylinder in the half-way plane) of radius R. This of course is guaranteed if the furthest point of the molecular projection is less than or equal to R. Hence the condition that a molecule be completely contained in the right circular cylindrical domain of radius R is given by the constraint $r_p \leqslant R$ and, due to equation (10b), this in turn is guaranteed by the condition

$$r_+(l, k, \theta) \leqslant R - r_0;$$

(11a)

this is the needed generalization of condition (5c) to the case $\theta \neq 0$. Note that by comparing equations (5b) and (8b) we find, as expected, that $\vec{r}_{+}(l, k, 0) = \vec{r}_{-}(l, k, 0) = \vec{r}(l, k, 0) = \vec{r}_{lk}(0)$. Thus, when $\theta = 0$, condition (11a) above reduces to condition (5c) as it should. The rest of the derivation follows essentially the same steps as in the case $\theta = 0$ (worked out in [7]) with $r_{lk}(0) = r(l, k, 0)$ replaced by $r_{+}(l, k, \theta)$ as given by equation (8b).

Since, on physical grounds, both sides of equation (11a) must be positive, the above constraint (11a) can be alternatively written as

$$\left(\frac{r_{+}(l, k, \theta)}{2r_0}\right)^2 - \left(\frac{R - r_0}{2r_0}\right)^2 \leqslant 0, \tag{11b}$$

or simply as

$$f_l(k, \theta) \leqslant 0, \tag{11c}$$

where, using equation (8b), $f_l(k, \theta)$ can be written as

$$f_l(k, \theta) = k^2 - lk - \eta_l(\theta) \tag{12a}$$

with $\eta_l(\theta)$ defined by

$$\eta_l(\theta) = \left(\frac{R - r_0}{2r_0}\right)^2 - \left(\frac{l}{2}\right)^2 - \frac{1}{4}\left[\frac{\sqrt{3}|l|}{\cos\theta} + \left(\frac{h}{2r_0}\right)\sin\theta\right]^2. \tag{12b}$$

For $\theta = 0$, expression (12) for $f_l(k, \theta)$ reduces to expression (34) of [7] for $f_l(k)$ as expected.

4.   Number of molecules in a domain

4.1. *The allowed values of* k

We have written $f_l(k, \theta)$ in such a way as to bring out its dependence on k and we treat l as a parameter. Since $f_l(k, \theta)$ is a second-order polynomial in k, and since the coefficient of k^2 is positive, then $f_l(k, \theta)$ is negative in between the roots of the polynomial. The roots of $f_l(k, \theta)$ are given by

$$k_{\pm}(l) = \frac{l \pm \sqrt{\Delta(|l|, \theta)}}{2}, \tag{13a}$$

where

$$\Delta(|l|, \theta) = \left(\frac{R}{r_0} - 1\right)^2 - \left(\frac{\sqrt{3}|l|}{\cos\theta} + \frac{h\sin\theta}{2r_0}\right)^2. \tag{13b}$$

Thus constraint (11c), guaranteeing that the molecule is inside the domain, can be rewritten as

$$k_{-} \leqslant k \leqslant k_{+}, \tag{14a}$$

and since k is integer, then the allowed range of values of k is

$$k_{\min} \leqslant k \leqslant k_{\max}, \tag{14b}$$

where

$$k_{\min} = [k_-]^+ = \left[\frac{l - \sqrt{\Delta(|l|, \theta)}}{2}\right]^+ \quad \text{and} \quad k_{\max} = [k_+]^- = \left[\frac{l + \sqrt{\Delta(|l|, \theta)}}{2}\right]^-. \tag{14c}$$

As defined in [7], $[x]^+$ is the smallest integer greater or equal to x (ceiling of x), and $[x]^-$ is the largest integer smaller or equal to x (floor of x). For $\theta = 0$, expression (13b) for $\Delta(|l|, \theta)$ reduces, as expected, to expression (36) of [7] for Δ.

4.2. The allowed values of l

The allowed values of l are those for which $\Delta(|l|, \theta)$ is positive. From equation (13b) it is seen that $\Delta(|l|, \theta)$ is a second-order polynomial in $|l|$ and the coefficient of $|l|^2$ is negative. Hence $\Delta(|l|, \theta)$ is positive for values of $|l|$ which are in between the roots of the polynomial. Let $|l|_<$ be the smaller, and $|l|_>$ the larger of the two roots. Then the allowed values of $|l|$ for which $\Delta(|l|, \theta)$ is positive are given by the two simultaneous conditions:

$$|l|_< \leqslant |l| \leqslant |l|_> \tag{15a}$$

and

$$|l| \geqslant 0. \tag{15b}$$

The roots of $\Delta(|l|, \theta)$ are easily obtained in the form

$$|l|_\pm = \left[\pm 2(R - r_0) - h \sin\theta\right] \frac{\cos\theta}{2r_0\sqrt{3}}. \tag{16}$$

For equations (15a) and (15b) to have a simultaneous solution at least one of the two above roots must be positive. From physical considerations, the possible range of variation of θ is $0 \leqslant \theta \leqslant \pi/2$, and in this range both $\sin\theta$ and $\cos\theta$ are non-negative. Hence, to avoid having two negative roots, the second term on the right in equation (16) must not be the dominant term, that is, we must have

$$2R \geqslant h \sin\theta + 2r_0. \tag{17}$$

This condition is physically understandable since it requires that the diameter of the projection of the domain cylinder on the half-way plane be larger than the total length of the projection of a molecule on the half-way plane. Once condition (17) is satisfied, then we have

$$|l|_< = |l|_- \leqslant 0, \tag{18a}$$

$$|l|_> = |l|_+ \geqslant 0. \tag{18b}$$

Combining equations (15a), (15b) and (18a), (18b) leads to the condition

$$0 \leqslant |l| \leqslant |l|_+. \tag{19}$$

This condition can be made more explicit by defining $p(\theta)$ as the largest allowed value of $|l|$; then

$$p(\theta) = |l|_{\max} = \left[|l|_+\right]^- = \left[\frac{\cos\theta}{\sqrt{3}}\left(\frac{R}{r_0} - 1 - \frac{h\sin\theta}{2r_0}\right)\right]^-, \tag{20a}$$

and the allowed range of values of l (when (17) is satisfied) is

$$-p(\theta) \leqslant l \leqslant p(\theta). \tag{20b}$$

For $\theta = 0$, expression (20a) for $p(\theta)$ reduces, as expected, to expression (42) of [7] for p.

4.3. The number of molecules

The number of molecules in the domain is the number of occupied lattice sites. There is one lattice site for every allowed pair of values (l, k). The allowed values of l are given via equation (20), and for every allowed value of l the number $N_l(R, \theta)$ of allowed values of k is given via equation (14) by

$$N_l(R, \theta) = k_{\max} - k_{\min} + 1 = \left[k_+(l)\right]^- - \left[k_-(l)\right]^+ + 1, \tag{21a}$$

where $k_\pm(l)$ are given by equations (13a) and (13b). Making use of the fact that $k_-(-l) = -k_+(l)$, $[-x]^+ = -[x]^-$, and $[-x]^- = -[x]^+$, it is straight forward to show (using equation (14c)) that

$$N_l(R, \theta) = N_{-l}(R, \theta). \tag{21b}$$

Substituting for $k_\pm(l)$ their values as given by (13a) and making use again of the identity $[-x]^+ = -[x]^-$, equation (21a) becomes

$$N_l(R, \theta) = \left[\frac{\sqrt{\Delta(|l|, \theta)} + l}{2}\right]^- + \left[\frac{\sqrt{\Delta(|l|, \theta)} - l}{2}\right]^- + 1. \tag{21c}$$

Equation (21c) gives the number of molecules corresponding to an allowed value of l. The total number $N(R, \theta)$ of molecules of inclination θ in a domain of radius R is obtained by summing $N_l(R, \theta)$ over all allowed values of l. Hence,

$$N(R, \theta) = \sum_{l=-p(\theta)}^{p(\theta)} N_l(R, \theta). \tag{22a}$$

Making use of equation (21b), this can be rewritten as

$$N(R, \theta) = N_0(R, \theta) + 2\sum_{l=1}^{p(\theta)} N_l(R, \theta). \tag{22b}$$

Substituting for $N_l(R, \theta)$ its value as given by equation (21c), summing over the factor unity that appears in (21c), and making use of expression (20a) for $p(\theta)$, the above equation can be rewritten as

$$N(R, \theta) = 1 + 2\left[\frac{1}{2}\sqrt{\Delta(0, \theta)}\right]^- + 2\left[\frac{\cos\theta}{\sqrt{3}}\left(\frac{R}{r_0} - 1 - \frac{h\sin\theta}{2r_0}\right)\right]^-$$
$$+ 2\sum_{l=1}^{p(\theta)}\left\{\left[\frac{1}{2}\left(\sqrt{\Delta(|l|, \theta)} + l\right)\right]^- + \left[\frac{1}{2}\left(\sqrt{\Delta(|l|, \theta)} - l\right)\right]^-\right\}. \quad (22c)$$

Written out explicitly, using expression (13b) for $\Delta(|l|, \theta)$, the above equation becomes

$$N(R, \theta) = 1 + 2\left[\frac{1}{2}\sqrt{\left(\frac{R}{r_0} - 1\right)^2 - \left(\frac{h\sin\theta}{2r_0}\right)^2}\right]^- + 2\left[\frac{\cos\theta}{\sqrt{3}}\left(\frac{R}{r_0} - 1 - \frac{h\sin\theta}{2r_0}\right)\right]^-$$
$$+ 2\sum_{l=1}^{p(\theta)}\left[\frac{1}{2}\left\{\sqrt{\left(\frac{R}{r_0} - 1\right)^2 - \left(\frac{\sqrt{3}|l|}{\cos\theta} + \frac{h\sin\theta}{2r_0}\right)^2} + l\right\}\right]^-$$
$$+ 2\sum_{l=1}^{p(\theta)}\left[\frac{1}{2}\left\{\sqrt{\left(\frac{R}{r_0} - 1\right)^2 - \left(\frac{\sqrt{3}|l|}{\cos\theta} + \frac{h\sin\theta}{2r_0}\right)^2} - l\right\}\right]^-. \quad (22d)$$

Once $N(R, \theta)$ is evaluated, the packing fraction β is readily obtained via equation (3h).

Expression (22d) for $N(R, \theta)$ provides a solution for the problem of packing of spherocylindrical molecules in a right circular cylindrical domain, when the molecules are inclined at an angle θ to the cylinder axis. When the plane of inclination is the zx-plane (as defined above) the solution is exact. For inclinations in other directions minor corrections need to be introduced. These go beyond the scope of this paper and will be dealt with subsequently.

How much detail one needs to keep in evaluating equation (22b) depends on the problem at hand. In the next section we will discuss the simplifying approximations that can be introduced when the number of molecules in a domain is large.

5.   Domains with a large number of molecules

The summond in equation (22a) for $N(R, \theta)$ is $N_l(R, \theta)$, and from equation (21c) this is seen to be essentially equal to $\sqrt{\Delta(|l|, \theta)}$. From equation (13b) it is seen that $\Delta(|l|, \theta)$ increases with increasing values of R/r_0, while it decreases with increasing values of $h\sin\theta/r_0$ and increasing values of θ (in the range $0 \leqslant \theta \leqslant \pi/2$ of course). Furthermore, $\Delta(|l|, \theta)$ is maximum for $l = 0$ and decreases monotonically with increasing $|l|$ to approximately zero for $|l| = |l|_{\max} = p(\theta)$. The greater the value of $p(\theta)$ the larger the sum. As seen from equation (20a), $p(\theta)$ is also positively correlated to R/r_0 and negatively correlated $h\sin\theta/r_0$ and to θ. Hence we conclude that for the

domain to have a large number of molecules, the following three conditions must be satisfied:

(i) $R/r_0 \gg 1$,

(ii) $R/r_0 \gg h \sin \theta / r_0$,

(iii) θ not too large.

5.1. Successive approximations

Once the above conditions, guaranteeing that $N(R, \theta) \gg 1$, are met, a number of approximations, simplifying the evaluation of equation (22a), become justified, and will be introduce one at a time. As we proceed through the successive approximations the expression for $N(R, \theta)$ simplifies progressively. In order to clearly delimit the range of validity of the successive expressions for $N(R, \theta)$ (and, consequently, permit maximum flexibility in the use of the results obtained here), we will clearly specify each approximation and its partial contribution towards the final result.

5.1.1. Integration

As a first simplification we approximate the sum in equation (18a) by an integral

$$\sum_{l=-p(\theta)}^{p(\theta)} \Rightarrow \int_{-p(\theta)}^{p(\theta)} \mathrm{d}l.$$

Hence, $N(R, \theta)$ is approximated by

$$N(R, \theta) \approx \int_{-p(\theta)}^{p(\theta)} N_l(R, \theta) \, \mathrm{d}l, \tag{23a}$$

and making use of the symmetry properties of $N_l(R, \theta)$ as expressed by equation (21b), this can be rewritten as

$$N(R, \theta) \approx 2 \int_{0}^{p(\theta)} N_l(R, \theta) \, \mathrm{d}l. \tag{23b}$$

5.1.2. Smoothing

As discussed in [7], for large values of the argument of the "floor" and "ceiling" operators, $[\,]^-$ and $[\,]^+$, respectively, we may use the approximations $[\,]^- \approx [\,] - 1/2$ and $[\,]^+ \approx [\,] + 1/2$. Applying these approximations to equations (20a) and (21c) we obtain

$$p(\theta) \approx \frac{\cos \theta}{\sqrt{3}} \left(\frac{R}{r_0} - 1 - \frac{h \sin \theta}{2 r_0} \right) - \frac{1}{2} \tag{24a}$$

and

$$N_l(R, \theta) \approx \sqrt{\Delta\big(|l|, \theta\big)}. \tag{24b}$$

Combining equations (23b) and (24b) and making use of the explicit expression for $\Delta(|l|, \theta)$, as given by equation (13b), equation (22a) reduces to

$$N(R, \theta) \approx 2 \int_0^{p(\theta)} dl \sqrt{\Delta(|l|, \theta)} \approx 2 \int_0^{p(\theta)} dl \sqrt{\left(\frac{R}{r_0} - 1\right)^2 - \left(\frac{\sqrt{3}l}{\cos\theta} + \frac{h\sin\theta}{2r_0}\right)^2},$$
(25)

where, under the integral sign, we replaced $|l|$ by l in the expression for $\Delta(|l|, \theta)$. This is permitted since the integral ranges exclusively over non-negative values of l.

To perform the integration it is convenient to make the change of variable

$$l \to x(l) = \frac{\sqrt{3}}{\cos\theta} l + \left(\frac{h\sin\theta}{2r_0}\right), \quad dx = \frac{\sqrt{3}}{\cos\theta} dl;$$
(26a)

then

$$N(R, \theta) \approx \frac{2\cos\theta}{\sqrt{3}} \int_a^b dx \sqrt{\left(\frac{R}{r_0} - 1\right)^2 - x^2},$$
(26b)

with

$$a = x(0) = \frac{h\sin\theta}{2r_0}$$
(26c)

and

$$b = x(p(\theta)) = \frac{R}{r_0} - 1 - \frac{\sqrt{3}}{2\cos\theta}.$$
(26d)

Performing the above integration we obtain after some algebraic manipulation (see appendix A)

$$
\begin{aligned}
N(R, \theta) \approx & \left[\left(\frac{R}{r_0} - 1\right) - \frac{\sqrt{3}}{2\cos\theta}\right]\left(\frac{R}{r_0} - 1\right)^{1/2} \sqrt{\frac{\cos\theta}{\sqrt{3}}\left(1 - \frac{\sqrt{3}r_0}{4(R - r_0)\cos\theta}\right)} \\
& - \frac{h\sin\theta\cos\theta}{2\sqrt{3}r_0}\left(\frac{R}{r_0} - 1\right)\sqrt{1 - \left(\frac{h\sin\theta}{2(R - r_0)}\right)^2} \\
& + \frac{\cos\theta}{\sqrt{3}}\left(\frac{R}{r_0} - 1\right)^2 \sin^{-1}\left\{\left[1 - \frac{r_0\sqrt{3}}{2(R - r_0)\cos\theta}\right]\sqrt{1 - \left(\frac{h\sin\theta}{2(R - r_0)}\right)^2}\right. \\
& \left. - \frac{h\sin\theta}{2(R - r_0)}\left(\frac{r_0\sqrt{3}}{(R - r_0)\cos\theta}\right)^{1/2}\sqrt{1 - \frac{r_0\sqrt{3}}{4(R - r_0)\cos\theta}}\right\}.
\end{aligned}
$$
(27)

5.1.3. Binomial
We now apply the binomial approximation

$$\sqrt{1 - \alpha} \underset{\alpha \ll 1}{\approx} 1 - \alpha/2$$

to all the square root expressions in equation (27) to obtain (again after some algebraic manipulation)

$$
N(R,\theta) \approx \left(\frac{R}{r_0} - 1\right)^2 \left(\frac{\cos\theta}{\sqrt{3}}\right) \sin^{-1}\left(1 - \varepsilon^2\right) + \left(\frac{R}{r_0} - 1\right)^{3/2} \left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2}
$$

$$
- \left(\frac{R}{r_0} - 1\right) \left(\frac{h\sin\theta}{2r_0}\right) \left(\frac{\cos\theta}{\sqrt{3}}\right) - \frac{5}{8}\left(\frac{R}{r_0} - 1\right)^{1/2} \left(\frac{\cos\theta}{\sqrt{3}}\right)^{-1/2}
$$

$$
+ \frac{1}{16}\left(\frac{R}{r_0} - 1\right)^{-1/2} \left(\frac{\cos\theta}{\sqrt{3}}\right)^{-3/2} + \frac{1}{2}\left(\frac{R}{r_0} - 1\right)^{-1} \left(\frac{h\sin\theta}{2r_0}\right)^3 \left(\frac{\cos\theta}{\sqrt{3}}\right),
$$

$$\tag{28a}$$

where, with the exception of the $\sin^{-1}$ term, the expression for $N(R,\theta)$ is written as a polynomial in $\sqrt{(R/r_0 - 1)}$. The value of ε^2 in the $\sin^{-1}$ term lies in the range $0 < \varepsilon^2 \ll 1$ and is given by

$$
\varepsilon = \frac{1}{\sqrt{2}}\left(\frac{r_0}{R - r_0}\right)^{1/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{1/2} \sqrt{1 + \xi}, \tag{28b}
$$

where ξ is defined as

$$
\xi = 2\left(\frac{r_0}{R - r_0}\right)^{1/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{-1/2} \left(\frac{h\sin\theta}{2r_0}\right) + \left(\frac{r_0}{R - r_0}\right) \left(\frac{\sqrt{3}}{\cos\theta}\right)^{-1} \left(\frac{h\sin\theta}{2r_0}\right)^2
$$

$$
- \frac{1}{4}\left(\frac{r_0}{R - r_0}\right)^{3/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{1/2} \left(\frac{h\sin\theta}{2r_0}\right) - \frac{1}{2}\left(\frac{r_0}{R - r_0}\right)^2 \left(\frac{h\sin\theta}{2r_0}\right)^2. \tag{28c}
$$

Applying the binomial approximation once more, this time to the expression for ε, we obtain

$$
\varepsilon \approx \frac{1}{\sqrt{2}}\left(\frac{r_0}{R - r_0}\right)^{1/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{1/2} \left(1 + \frac{1}{2}\xi\right), \tag{29a}
$$

or, explicitly,

$$
\varepsilon \approx \frac{1}{\sqrt{2}}\left(\frac{r_0}{R - r_0}\right)^{1/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{1/2} + \frac{1}{\sqrt{2}}\left(\frac{r_0}{R - r_0}\right) \left(\frac{h\sin\theta}{2r_0}\right)
$$

$$
+ \frac{1}{2\sqrt{2}}\left(\frac{r_0}{R - r_0}\right)^{3/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{-1/2} \left(\frac{h\sin\theta}{2r_0}\right)^2
$$

$$
- \frac{1}{8\sqrt{2}}\left(\frac{r_0}{R - r_0}\right)^2 \left(\frac{\sqrt{3}}{\cos\theta}\right) \left(\frac{h\sin\theta}{2r_0}\right)
$$

$$
- \frac{1}{4\sqrt{2}}\left(\frac{r_0}{R - r_0}\right)^{5/2} \left(\frac{\sqrt{3}}{\cos\theta}\right)^{1/2} \left(\frac{h\sin\theta}{2r_0}\right)^2. \tag{29b}
$$

5.1.4. Trigonometric

For small values of $0 \leqslant \varepsilon \ll 1$ we have $\sin(\pi/2 - \varepsilon) = \cos\varepsilon \approx 1 - \varepsilon^2$ and, hence,

$$\left(\frac{\pi}{2} - \varepsilon\right) \approx \sin^{-1}\left(1 - \varepsilon^2\right). \tag{30}$$

Thus the expression for $N(R, \theta)$ becomes

$$
\begin{aligned}
N(R, \theta) \approx{}& \left(\frac{R}{r_0} - 1\right)^2 \left(\frac{\cos\theta}{\sqrt{3}}\right)\left(\frac{\pi}{2} - \varepsilon\right) + \left(\frac{R}{r_0} - 1\right)^{3/2}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2} \\
& - \left(\frac{R}{r_0} - 1\right)\left(\frac{h\sin\theta}{2r_0}\right)\left(\frac{\cos\theta}{\sqrt{3}}\right) - \frac{5}{8}\left(\frac{R}{r_0} - 1\right)^{1/2}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{-1/2} \\
& + \frac{1}{16}\left(\frac{R}{r_0} - 1\right)^{-1/2}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{-3/2} + \frac{1}{2}\left(\frac{R}{r_0} - 1\right)^{-1}\left(\frac{h\sin\theta}{2r_0}\right)^3\left(\frac{\cos\theta}{\sqrt{3}}\right).
\end{aligned}
\tag{31a}
$$

Substituting for ε its explicit approximate value as given by equation (29b), we obtain $N(R, \theta)$ in the form

$$
\begin{aligned}
N(R, \theta) \approx{}& \left(\frac{R}{r_0} - 1\right)^2\left(\frac{\cos\theta}{\sqrt{3}}\right)\left(\frac{\pi}{2}\right) + \left(\frac{R}{r_0} - 1\right)^{3/2}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2}\left(1 - \frac{1}{\sqrt{2}}\right) \\
& - \left(\frac{R}{r_0} - 1\right)\left(\frac{\cos\theta}{\sqrt{3}}\right)\left(\frac{h\sin\theta}{2r_0}\right)\left(1 + \frac{1}{\sqrt{2}}\right) \\
& - \left(\frac{R}{r_0} - 1\right)^{1/2}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2}\left\{\frac{5}{8}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{-1} + \frac{1}{2\sqrt{2}}\left(\frac{h\sin\theta}{2r_0}\right)^2\right\} \\
& + \frac{1}{8\sqrt{2}}\left(\frac{h\sin\theta}{2r_0}\right) \\
& + \left(\frac{R}{r_0} - 1\right)^{-1/2}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2}\left\{\frac{1}{16}\left(\frac{\cos\theta}{\sqrt{3}}\right)^{-2} + \frac{1}{4\sqrt{2}}\left(\frac{h\sin\theta}{2r_0}\right)^2\right\} \\
& + \frac{1}{2}\left(\frac{R}{r_0} - 1\right)^{-1}\left(\frac{h\sin\theta}{2r_0}\right)^3\left(\frac{\cos\theta}{\sqrt{3}}\right).
\end{aligned}
\tag{31b}
$$

Finally, we have an expression for $N(R, \theta)$ which is truly a polynomial in $\sqrt{(R/r_0 - 1)}$.

5.2. Limiting cases

We now consider a number of important limiting cases. They will all be treated within the context of the approximations considered above. That is the starting point is expression (31b) above for $N(R, \theta)$.

5.2.1. Very large domains

For $R/r_0 \gg 1$, it is certainly permitted to keep only positive powers of $(R/r_0 - 1)$ and to set $(R/r_0 - 1) \approx R/r_0$. This is still a very conservative approximation. The resulting expression for $N(R, \theta)$ is

$$
\begin{aligned}
N(R, \theta) \approx & \left(\frac{R}{r_0}\right)^2 \left(\frac{\cos\theta}{\sqrt{3}}\right) \left(\frac{\pi}{2}\right) + \left(\frac{R}{r_0}\right)^{3/2} \left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2} \left(1 - \frac{1}{\sqrt{2}}\right) \\
& - \left(\frac{R}{r_0}\right) \left(\frac{\cos\theta}{\sqrt{3}}\right) \left(\frac{h\sin\theta}{2r_0}\right) \left(1 + \frac{1}{\sqrt{2}}\right) \\
& - \left(\frac{R}{r_0}\right)^{1/2} \left(\frac{\cos\theta}{\sqrt{3}}\right)^{1/2} \left\{ \frac{5}{8} \left(\frac{\cos\theta}{\sqrt{3}}\right)^{-1} + \frac{1}{2\sqrt{2}} \left(\frac{h\sin\theta}{2r_0}\right)^2 \right\}. \quad (32)
\end{aligned}
$$

5.2.2. Extremely large domains

In the limit $R/r_0 \to \infty$, we keep only the leading term in $(R/r_0 - 1) \approx R/r_0$, and $N(R, \theta)$ goes asymptotic as

$$
N(R, \theta) \approx \frac{\pi}{2\sqrt{3}} \left(\frac{R}{r_0}\right)^2 \cos\theta. \quad (33)
$$

This is the hexagonal packing factor for inclined molecules, and all effects due to the finite extension of the domain have disappeared. This, of course, is normal since we are taking the limit $R/r_0 \to \infty$. For $\theta = 0$, the above expression reduces to equation (52) of [7].

5.2.3. Small angle of inclination

For small values of θ, we have $\cos\theta \approx 1$ and $\sin\theta \approx \theta$; hence

$$
N(R, \theta) \approx A_0 - \theta B_0, \quad (34a)
$$

where we have neglected second-order terms in θ and where the coefficients A_0 and B_0 are given by

$$
\begin{aligned}
A_0(R/r_0) = & \left(\frac{R}{r_0} - 1\right)^2 \left(\frac{\pi}{2\sqrt{3}}\right) + \left(\frac{R}{r_0} - 1\right)^{3/2} \left(\frac{1}{\sqrt{3}}\right)^{1/2} \left(1 - \frac{1}{\sqrt{2}}\right) \\
& - \left(\frac{R}{r_0} - 1\right)^{1/2} (\sqrt{3})^{1/2} \left(\frac{5}{8}\right) \quad (34b)
\end{aligned}
$$

and

$$
B_0(R/r_0, h) = \left(\frac{R}{r_0} - 1\right) \left(\frac{h}{2r_0}\right) \left(\frac{1}{\sqrt{3}}\right) \left(1 + \frac{1}{\sqrt{2}}\right). \quad (34c)
$$

5.2.4. Short molecules

For small values of h/r_0, we keep only the first order terms in $(h \sin \theta / 2r_0)$, and expression (31b) for $N(R, \theta)$ reduces to

$$N(R, \theta) \approx A_1 - \left(\frac{h}{r_0} \right) B_1, \tag{35a}$$

where

$$A_1(R/r_0, \cos \theta) \approx \left(\frac{R}{r_0} - 1 \right)^2 \left(\frac{\cos \theta}{\sqrt{3}} \right) \left(\frac{\pi}{2} \right) + \left(\frac{R}{r_0} - 1 \right)^{3/2} \left(\frac{\cos \theta}{\sqrt{3}} \right)^{1/2} \left(1 - \frac{1}{\sqrt{2}} \right)$$
$$- \left(\frac{R}{r_0} - 1 \right)^{1/2} \left(\frac{\cos \theta}{\sqrt{3}} \right)^{-1/2} \left(\frac{5}{8} \right) \tag{35b}$$

and

$$B_1(R/r_0, \theta) = \left(\frac{R}{r_0} - 1 \right) \left(\frac{\cos \theta \sin \theta}{2\sqrt{3}} \right) \left(1 + \frac{1}{\sqrt{2}} \right). \tag{35c}$$

6.   Results and discussion

The packing fraction β is obtained from the number $N(R, \theta)$ of molecules in a domain. The number $N(R, \theta)$ is, in turn, calculated as a function of three dimensionless parameters:

 (i) R/r_0 giving the domain radius in unites of r_0;

 (ii) h/r_0 giving the length of the cylindrical part of the molecule in units of r_0; and

(iii) θ the angle of inclination of the molecular axes with respect to the normal to the interface.

Thus the length scale is set by the molecular radius r_0 (the radius of the cylindrical part of the molecule).

In the present work, the rod-like spherocylindrical molecules are taken to be "elementary" immutable building blocks. Non the less, in order to get a feeling for the range of possible values of h/r_0 we need to look inside the molecule, as shown in figure 7. The molecule is modeled in accordance with the "body-filled model" or equivalently the "hard sphere model". As can easily be seen from figure 7, the length of the cylindrical part of the molecule is

$$h = r_C \left[1 + 2(n - 1) \sin \frac{\alpha}{2} \right], \tag{36a}$$

and the radius of the cylindrical part of the molecule is

$$r_0 = 2r_C \cos \frac{\alpha}{2} + r_H \left(1 + \cos \frac{\alpha}{2} \right). \tag{36b}$$
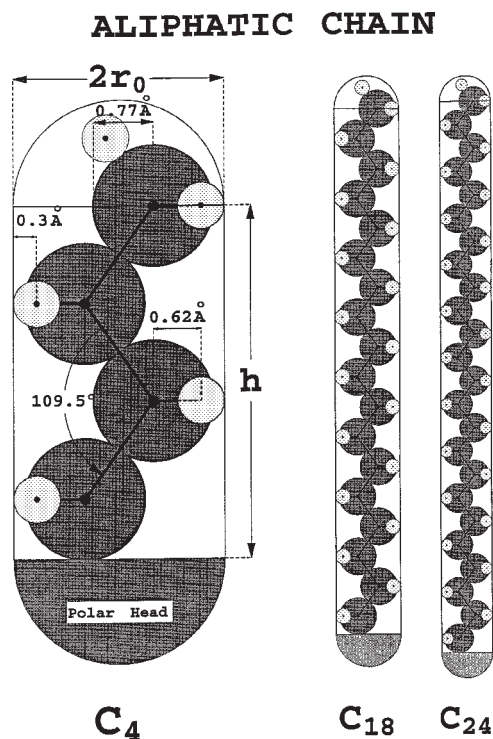
ALIPHATIC CHAIN

Figure 7. The relation between atomic and molecular parameters in the spherocylindrical molecular model. The model used is that of hard spheres (or body-filled). The values of single-bond covalent radii of hydrogen and carbon are $r_H = 0.3$ Å and $r_C = 0.77$ Å, respectively. The inter atomic distance is equal to the sum of the radii. The carbon atoms of the aliphatic chain are coplanar. The H–C–H bonds lie in planes that are perpendicular to the plane of the carbon backbone chain. The C–C–C and H–C–H angles are both $\alpha = 109.5°$. The organic molecules of biological interest have somewhere in-between 18 and 24 carbon atoms in their aliphatic chain (see table 1).

Here r_H and r_C are the single-bonded covalent radii of hydrogen and carbon atoms, respectively, α is the tetrahedral angle, and n is the number of carbon atoms in the aliphatic chain. Combining equations (36a) and (36b) we obtain

$$\frac{h}{r_0} = \frac{1 + 2(n-1)\tan(\alpha/2)}{2 + (r_H/r_C)(1 + \sec(\alpha/2))}. \tag{36c}$$

According to Pauling and Hayward [9], the values of single-bond covalent radii of hydrogen and carbon are $r_H = 0.3$ Å and $r_C = 0.77$ Å, respectively. Furthermore, the inter atomic distance for two atoms connected by a single bond is approximately equal to the sum of their covalent radii. The carbon atoms of the aliphatic chain are coplanar [5], while the H–C–H bonds lie in planes that are perpendicular to the plane of the carbon backbone chain. The C–C–C angle [8], as well as the H–C–H angle [10], are both those of a regular tetrahedron and have the characteristic value $\alpha = 109.5°$. The above numerical values are those used in figure 7 to "construct" the

Table 1
Spherocylindrical molecular parameters of some organically important molecules.

Lipid	Formula	C#	r_0	h	h/r_0
Lead stearate	$CH_3(CH_2)_{16}–CO_2Pb$	18	1.36	22.1	16.3
Stearic acid	$CH_3(CH_2)_{16}–CO_2H$	18	1.36	22.1	16.3
Arachidic acid	$CH_3(CH_2)_{18}–CO_2H$	20	1.36	24.7	18.1
Docosanoic acid	$CH_3(CH_2)_{20}–CO_2H$	22	1.36	27.2	20
Lignoseric acid	$CH_3(CH_2)_{22}–CO_2H$	24	1.36	29.7	21.8

C# is the number of carbon atoms in the molecule. r_0 and h are the radius and height of the molecular cylinder, respectively (as shown in figure 7), and they are both measured in angstroms.

rod-like spherocylindrical molecule. They lead to a molecular radius having the value $r_0 = 1.36$ Å. The resulting molecular cross-section is $\sigma_0 = 5.81$ Å^2. These values are much lower than the $r_0 = 2.20–2.25$ Å and corresponding $\sigma_0 = 15.2–15.9$ Å^2 obtained in [7] using a CPK model. This would seem to indicate that estimates of loss of efficiency in packing (as deduced from a comparison with the experimental data of Kjaer et al. [3] as well as that of Dutta et al. [2]) is much more significant than had previously been suspected (see [7]). As will be seen shortly, within the context of the assumption made here of freely rotating domains, the static loss of efficiency of packing ("loss of area") increases sharply with increasing inclination of the molecular axes. There is, of course, also the dynamic loss due to mobility (temperature) super imposed on this static loss.

In the case of organic molecules of biological interest in Langmuir films [2–4,12], the number of carbon atoms in the aliphatic chain varies between 18 and 24 atoms. According to the above model this leads to values of h/r_0 which range from 16 and 22, as shown in table 1. We use this range of values of h/r_0 as a guide in numerical calculations, and take the value $h/r_0 = 20$ as a "standard" relative length of the cylindrical part of the molecule. That is the standardized molecule has a relative length of $d/r_0 = h/r_0 + 2 = 22$.

Figure 8 shows a graphic simulation [6] of the packing of spherocylindrical molecules inside a right circular cylindrical domain, for "standard" molecules ($h/r_0 = 20$), inclined at an angle $\theta = 40°$ to the normal (to the interface), inside a cylindrical domain of relative radius $R/r_0 = 15$. According to equation (32d) the domain contains 59 molecules and this is confirmed by the graphic simulation.

The inclination of the molecules (with respect to the normal to the interface) breaks the symmetry with respect to 4 out of the 6 axis of symmetry present in the $\theta = 0°$ case. The surviving axes of symmetry are the x- and y-axes, respectively. It is worthwhile noting that in the process of inclining the molecules, the axis of rotation was taken to coincide with one of the original axes of symmetry in the half-way plane (specifically the y-axis). It is precisely this choice (rotating about a symmetry axis in the half-way plane) which is responsible for the partial preservation of the original symmetry in the half-way plane. There in lies the main justification of working in

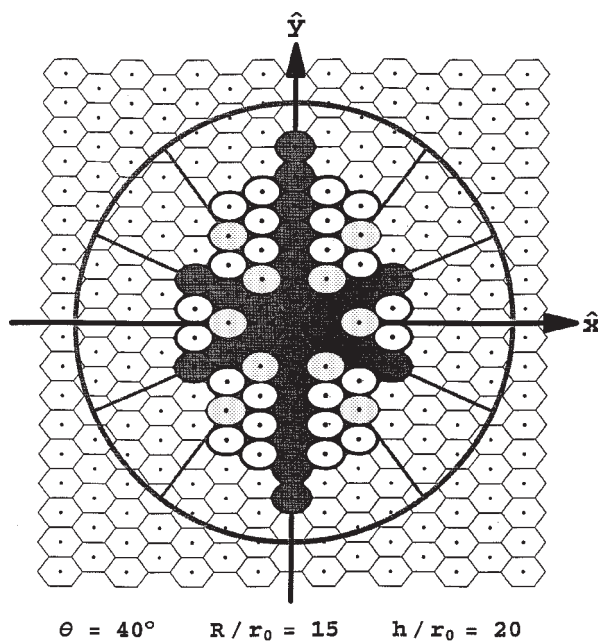$$\Theta = 40° \qquad R / r_0 = 15 \qquad h / r_0 = 20$$

Figure 8. Cross-section, in the half-way plane, of the hexagonally packed inclined molecules. The molecular projections that, in the limit $\theta = 0°$, will lie on a principal axes of symmetry are shown in black. Molecular projections that, in the limit $\theta = 0°$, will lie on a secondary axes of symmetry are shown in gray. When the inclining plane is the zx-plane, the x- and y-axes continue to be axes of symmetry of the lattice, but the remaining four axes shown loose this property.

(or rather projecting on) the half-way plane. Maximum symmetry leads to maximum entropy and hence this kind of inclination is favored statistically.

Figure 9 shows a graphic simulation of the variation of the packing with inclination angle and with relative domain radius, for a standardized molecule of relative length $d/r_0 = 22$. The values of $N(R,\theta)$ (the number of molecules in the domain) are calculated using equation (22d). It is seen that the loss of packing efficiency ("loss of area") due to boundary effects is substantial for large angles of inclination.

Figure 10 gives the number of molecules $N(R,\theta)$ as a function of domain radius for up to $R/r_0 = 50$. That is for domains of less than 2000 molecules. The discrete points on the graph are calculated using the exact expression for $N(R,\theta)$, as given by equation (22d). The continuous lines are evaluated using the analytical approximate expression (31b). The analytical expression (31b) is formally an approximation valid for large domains, and its accuracy increases with increasing domain radius. Two interesting facts emerge from figure 10: (i) the threshold value of R_N (for the domain radius R) at which the analytic approximation becomes essentially indistinguishable from the exact result (i.e., the threshold for "asymptotia") is surprisingly low when measured in unites of r_0, and (ii) this threshold value R_N increases with increasing angle of inclination. As θ varies from 0 to 40°, R_N/r_0 varies from about 10 to 20. These correspond to domains having a radius of somewhere in the range $R = 13$–27 Å.
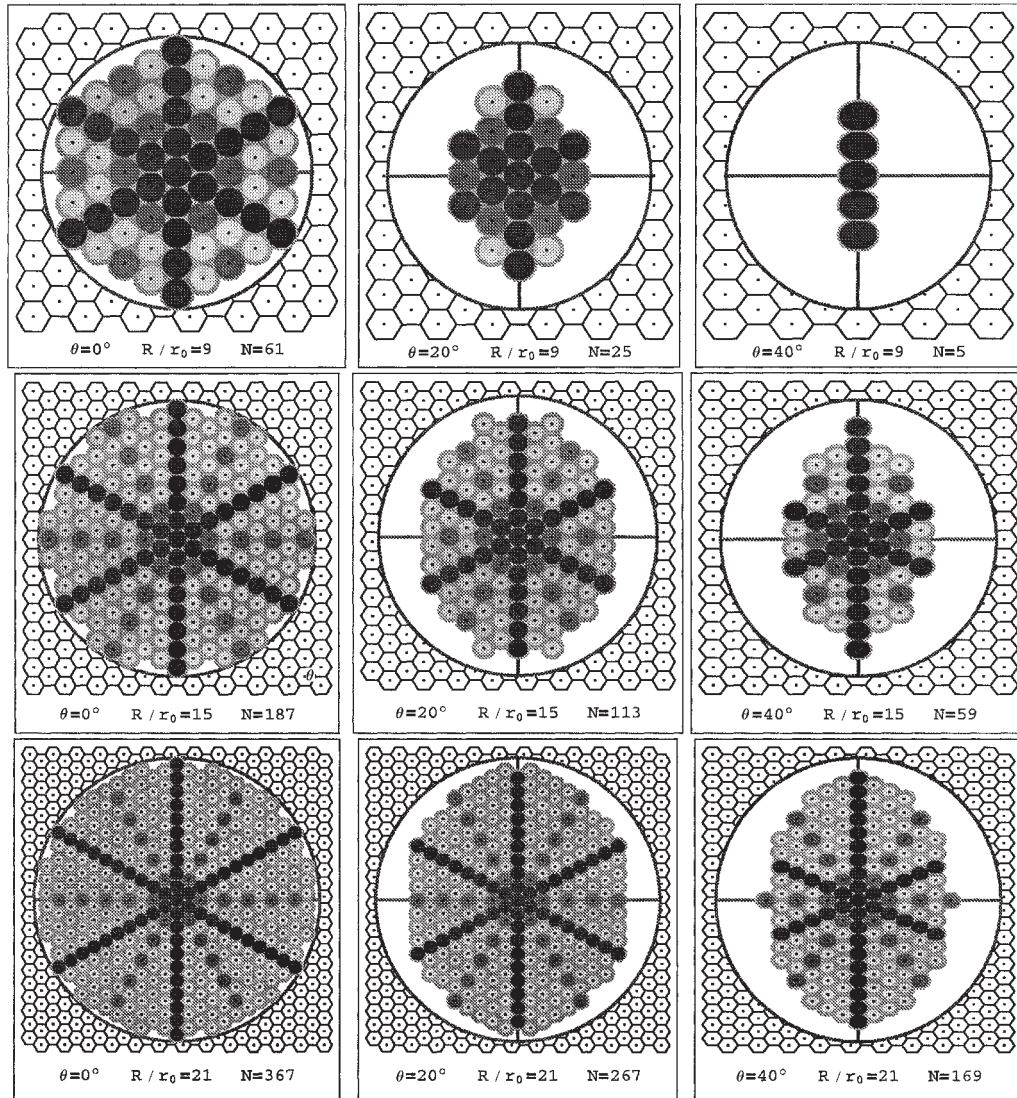
Figure 9. Packing of inclined molecules inside a cylindrical domain for various values of the "relative" domain size R/r_0, the "relative" molecular size h/r_0 and the inclination angle θ. The importance of the boundary effects for inclined molecules is clearly visible.

Figure 11 gives the packing fraction $\beta = N(R,\theta)(r_0/R)^2/\cos\theta$ as a function of domain radius for up to $R/r_0 = 50$. As in figure 10, the discrete points on the graph are calculated using the exact expression for $N(R,\theta)$, as given by equation (22d), while the continuous lines are evaluated using the approximate expression (31b). The expression for the packing fraction is more sensitive (then the expression for the number of molecules) to the difference between the exact and approximate forms of $N(R,\theta)$. For $\theta = 40°$ it is seen that the threshold R_β for the onset of the approximate
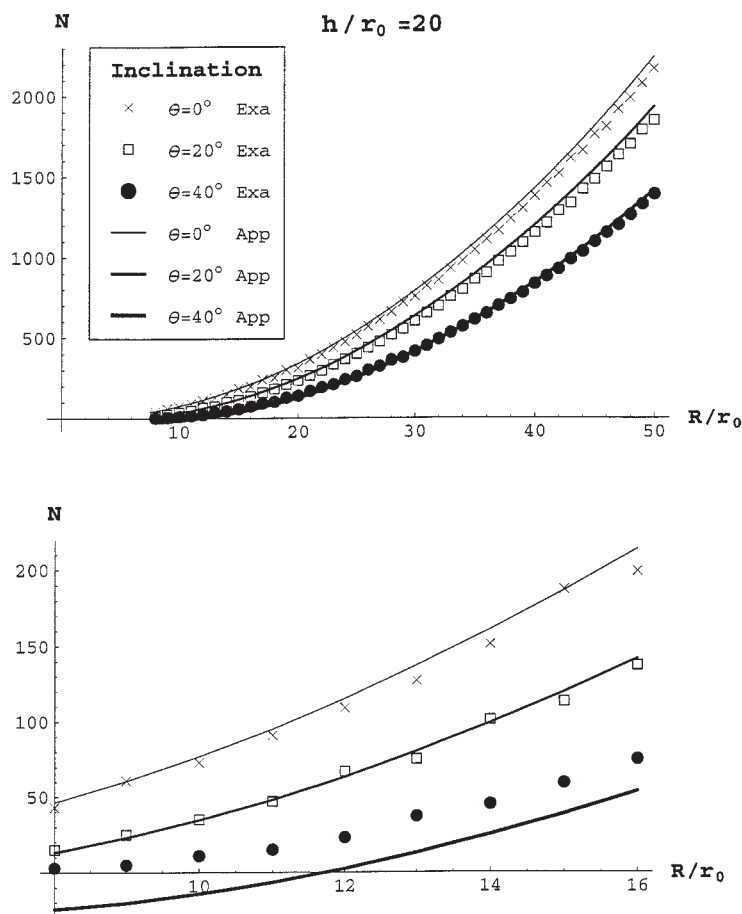
Figure 10. Number of molecules in a domain as a function of domain radius for various inclinations of the molecular axes. The discrete points are exact results calculated using equation (22d). The continuous lines are approximate results using the approximate interpolating function (31b).

expression is about $R_\beta = 40$ Å. It is also worth while noting that the "speed" at which the packing fraction asymptotically approaches the hexagonal limit of $\beta = 0.9 \sec \theta$ slows down with increasing angles of inclination.

Figure 12 analyses the contribution to $N(R, \theta)$ of the different terms, in the approximate analytic expression (31b), in order to determine how many terms is it really necessary to keep in different circumstances. The exact values of $N(R, \theta)$, as calculated from equation (22d), are shown as full black discs. The results obtained using the full analytic expression (7 terms), as given by equation (31b), are indicated by dark gray squares. The results obtained by keeping only the four leading terms in (31b) are indicated by black crosses, and the results obtained by keeping only the three leading terms in (31b) are indicated by pale gray discs. This figure is intended to serve as a guide for simplification depending on the needed accuracy.
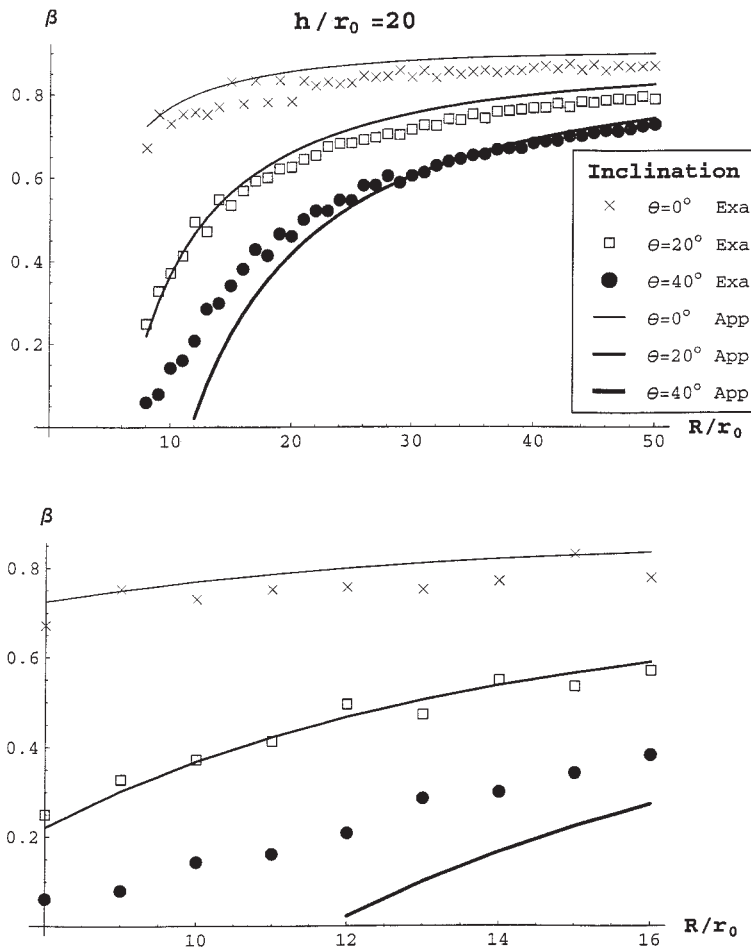
Figure 11. Packing fraction as a function of domain radius for various inclinations of the molecular axes. The discrete points are exact results calculated using equation (22d). The continuous lines are approximate results using the approximate interpolating function (31b).

7. Conclusion

We have calculated the impact of boundary effects on the hexagonal packing of spherocylindrical molecules inside a freely rotating cylindrical domain of a Langmuir film at the liquid–gas interface. The packing fraction is calculated as a function of the domain radius and the inclination of the molecules relative to the interface. The importance of the boundary effects increase rapidly with increasing angle of inclination. The analysis is static, thus establishing an upper bound on the packing fraction. Thermodynamical effects will lower this bound further. The analysis assumes symmetrical spherocylindrical molecules. Asymmetrical molecules will further lower this bound. Finally, the domains are assumed to be freely rotating. That implies that the interaction between domains is negligible and that every domain has sufficient rotational energy
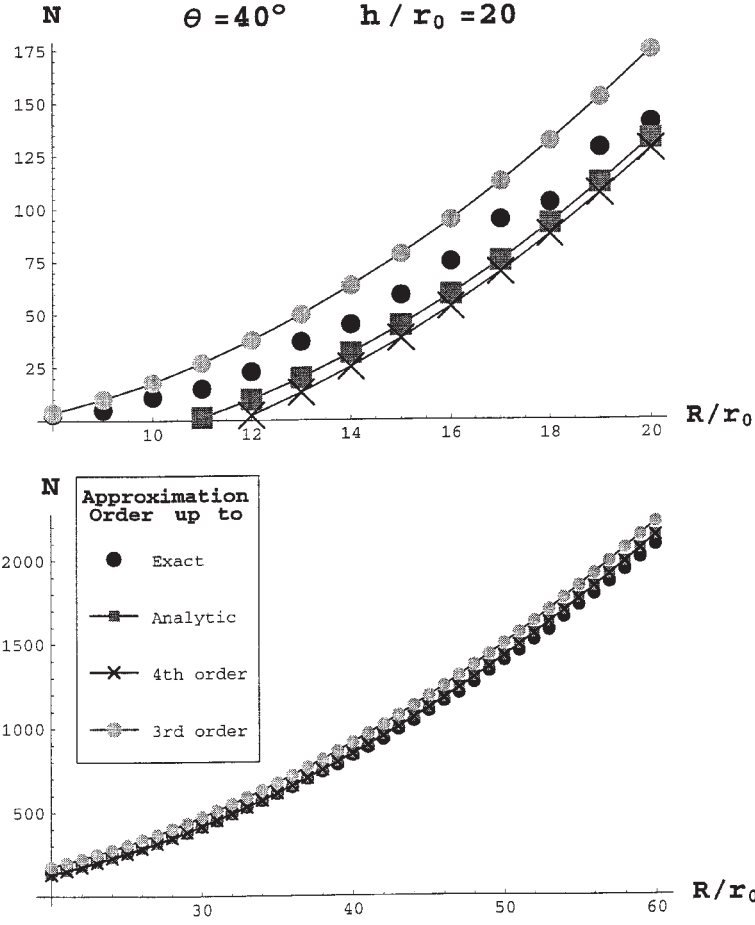
Figure 12. Number of molecules versus domain radius. A comparison of the exact result (black discs) as calculated via equation (22d), with different order approximations of the approximate analytic result (31b) (gray squares → full expression; black crosses → first four leading terms; pale gray discs → first three leading terms).

to protect its "territory" and have sufficient space to be able to rotate freely. This assumption will probably break down at some sufficiently low temperature.

The present work thus establishes a framework for studying thermodynamical effects. Within this framework, asymmetries in molecular shapes can be treated as perturbations.

Appendix A: The integral for $N(R, \theta)$

The integral that needs to be evaluated is

$$N(R, \theta) \approx \frac{2 \cos \theta}{\sqrt{3}} \int_a^b \mathrm{d}x \sqrt{\left(\frac{R}{r_0} - 1\right)^2 - x^2}, \qquad \text{(A.1a)}$$

with

$$a = x(0) = \frac{h \sin \theta}{2r_0} \tag{A.1b}$$

and

$$b = x\big(p(\theta)\big) = \frac{R}{r_0} - 1 - \frac{\sqrt{3}}{2 \cos \theta}. \tag{A.1c}$$

Our starting point is the two identities [11]:

$$\int dx \sqrt{\alpha^2 - x^2} = \frac{1}{2}\left(x\sqrt{\alpha^2 - x^2} + \alpha^2 \sin^{-1} \frac{x}{\alpha} \right) \tag{A.2}$$

and

$$\sin^{-1} y - \sin^{-1} x = \sin^{-1}\left(y\sqrt{1 - x^2} - x\sqrt{1 - y^2} \right). \tag{A.3}$$

Due to (A.2) we have

$$\int_a^b dx \sqrt{\alpha^2 - x^2} = \frac{1}{2}\left(b\sqrt{\alpha^2 - b^2} - a\sqrt{\alpha^2 - a^2} \right) + \frac{\alpha^2}{2}\left(\sin^{-1} \frac{b}{\alpha} - \sin^{-1} \frac{a}{\alpha} \right), \tag{A.4a}$$

and due to (A.3) we have

$$\sin^{-1} \frac{b}{\alpha} - \sin^{-1} \frac{a}{\alpha} = \sin^{-1}\left[\frac{b}{\alpha^2}\sqrt{\alpha^2 - a^2} - \frac{a}{\alpha^2}\sqrt{\alpha^2 - b^2} \right]. \tag{A.4b}$$

Combining the above two expressions we obtain

$$\int_a^b dx \sqrt{\alpha^2 - x^2} = \frac{1}{2}\left(b\sqrt{\alpha^2 - b^2} - a\sqrt{\alpha^2 - a^2} \right)$$
$$+ \frac{\alpha^2}{2} \sin^{-1}\left(\frac{b}{\alpha^2}\sqrt{\alpha^2 - a^2} - \frac{a}{\alpha^2}\sqrt{\alpha^2 - b^2} \right). \tag{A.5}$$

Applying the above identity to integral (A.1a) with $\alpha = (R/r_0 - 1)$ and the integration limits a and b given by equations (A.1b) and (A.1c), respectively, we obtain

$$N(R, \theta) \approx \frac{2 \cos \theta}{\sqrt{3}} \int_a^b dx \sqrt{\left(\frac{R}{r_0} - 1 \right)^2 - x^2}$$

$$= \frac{\cos \theta}{\sqrt{3}} \left\{ \left[\left(\frac{R}{r_0} - 1 \right) - \frac{\sqrt{3}}{2 \cos \theta} \right] \sqrt{\left(\frac{R}{r_0} - 1 \right)^2 - \left[\left(\frac{R}{r_0} - 1 \right) - \frac{\sqrt{3}}{2 \cos \theta} \right]^2} \right.$$

$$\left. - \left[\left(\frac{h}{2r_0} \right) \sin \theta \right] \sqrt{\left(\frac{R}{r_0} - 1 \right)^2 - \left[\left(\frac{h}{2r_0} \right) \sin \theta \right]^2} \right\}$$

$$+ \frac{\cos\theta}{\sqrt{3}} \left(\frac{R}{r_0} - 1 \right)^2 \sin^{-1} \left\{ \frac{[(R/r_0 - 1) - \sqrt{3}/(2\cos\theta)]}{(R/r_0 - 1)^2} \right.$$

$$\times \sqrt{ \left(\frac{R}{r_0} - 1 \right)^2 - \left[\left(\frac{h}{2r_0} \right) \sin\theta \right]^2 }$$

$$\left. - \frac{[(h/(2r_0)) \sin\theta]}{(R/r_0 - 1)^2} \sqrt{ \left(\frac{R}{r_0} - 1 \right)^2 - \left[\left(\frac{R}{r_0} - 1 \right) - \frac{\sqrt{3}}{2\cos\theta} \right]^2 } \right\}, \qquad \text{(A.6)}$$

which, after some straight forward algebraic manipulation, becomes equation (27) of the main text.

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