Tilting operator for phospholipidic molecular domains at the liquid–gas interface

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We derive a coordinate independent operator expression for the *tilting operator* of molecular domains at the liquid–gas interface. The domains are made up of phospholipidic molecules modeled as spherocylinders. The molecules of the domain are oriented parallel to each other. The centers of symmetry of the molecules form a lattice. The tilting operator keeps track of the deformations suffered by this lattice as the domain molecules are tilted relative to the normal to the interface. The results obtained are important for dynamic calculations of inclination dependent collective film characteristics, as in the simulation of surface density versus surface pressure curves in a Langmuir film. The tilting operation can be decomposed into three separate simple operations: a global rotation, a local oblique realignment, and a global vertical translation.

1.   Introduction

The molecules in a Langmuir film at the liquid–gas interface are organized in domains [4,6,8–10,12]. As a first approximation, the molecules in a domain may be considered to be identical, aligned parallel to each other, and collectively inclined at an angle θ with respect to the vertical (the normal to the liquid–gas interface). In [2,11] a distinction is made between the "physical domain" made up of the molecules, and the "virtual domain" made up of the circumscribing cylinder. As the molecules are tilted by an angle θ to the vertical, the base of the circumscribing cylinder increases while its height decreases, but its axis remains perpendicular to the interface. On the other hand, the physical domain tilts with the molecules and its cross-section in a plane perpendicular to interface is trapezoidal. The "virtual domain" is a measure of the space (or territory) that the physical domain occupies as it freely rotates.

Again within the context of a first approximation, the molecules of the domain may be taken to be spherocylindrical [3] and closely packed. The points of intersection of the symmetry axes of these molecules with a plane parallel to the interface form a lattice. The plane in which this lattice has maximum symmetry is situated half way in-between the base and the top of the virtual domain. This plane is referred to as

the half-way plane [2,11]. As the physical domain is tilted, the lattice in the half-way plane is deformed. It is convenient to have an operator that keeps track of this deformation as a function of the direction, and angle, of inclination. We refer to this operator as the *tilting operator*. Its derivation is the subject of the present work. Its power becomes apparent when one considers doing dynamic calculations of Langmuir film characteristics that are inclination dependent, as for example in the simulation of surface density versus surface pressure curves.

The tilting operation is complex and continuos, but it can be decomposed into three separate successive simple mutually commuting operations: (i) a global rotation of the physical domain about an axis in the halfway plane at a fixed height above the interface, in order to tilt the molecules relative to the normal to the interface; (ii) a local hydrophobic–hydrophilic driven oblique translation of the individual molecules, in order to realign their polar heads on a plane parallel to the interface; and (iii) a global vertical translation of the physical domain in order to compensate for the change in height of the circumscribing cylinder, thus bringing the half-way plane into position, and replacing the polar heads on the interface.

The first and second of the above operations can be expressed in terms of the generator of infinitesimal rotations. This is normal for the rotation operation [1], and is a consequence of the hydrophobic–hydrophilic forces acting locally for the oblique translation. This circumstance considerably simplifies the final form of the tilting operator. Thus, the local action of the hydrophobic–hydrophilic interaction, rather than complicating the result, actually simplifies it, adding to the interest of the tilting operator.

In section 2 we set up the molecular model of the domain and its mathematical representation. In section 3 we derive the tilting operator in a purely operator, coordinate independent, form. In section 4 we use this operator to obtain the resultant deformed lattice when an initially vertically aligned, and hexagonally close packed, domain is tilted.

2.   The model

Globally the system we are dealing with here presupposes phospholipidic molecules arranged in domains forming a Langmuir film at the liquid–gas interface, and that the centers of the molecules of a domain form a two-dimensional lattice. It also presupposes that the "external" hydrophobic and hydrophilic interaction between the molecules of the domain and the interface, dominate over the "residual" van der Waals interactions, due to boundary effects, in between the molecules of the domain. Thus the central features of the model are *regularity* and *hydro-dominance*. Regularity is equivalent to "embedding" the molecules of the domain in identical "virtual" spherocylindrical (rod-like) molecules that are aligned parallel to each other. Hydro-dominance is equivalent to allowing the molecules to slide freely along each other. It is generally a good approximation, and its precision improves with increasing molecular length and decreasing angle of inclination. An experimental measure of the accuracy of
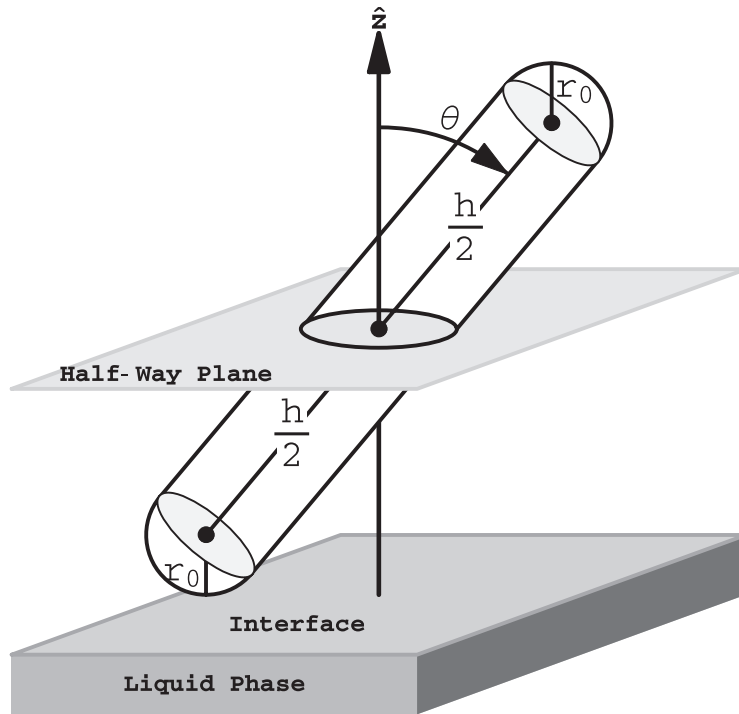
Figure 1. Parameters of the spherocylindrical model of a molecule at the liquid–gas interface. The $\widehat{z}$ axis is normal to the interface. The molecule is tilted by an angle θ to the normal. The length of the molecule is $d = h + 2r_0$.

the assumption of hydro-dominance is the average smoothness of the domain surfaces, and the precision with which they are individually parallel to the interface.

2.1. Static characteristics

We will here only give a summary of the essential features of the underlying static model and refer the reader to [2,11] for details and justification. The *molecules* in a domain are considered to be spherocylindrical [3,11] as shown in figure 1. The cylinders have radius r_0 and height h. The hemispheres have radius r_0. The total length d of a molecule is given by

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

The molecules are assumed to be all identical and aligned parallel to each other. They are collectively inclined at an angle θ to the vertical (the normal to the gas–liquid interface). The spherical polar heads of the molecules are tangent to a plane which is parallel to the interface. We refer to this ensemble of parallel molecules as the "*physical domain*".
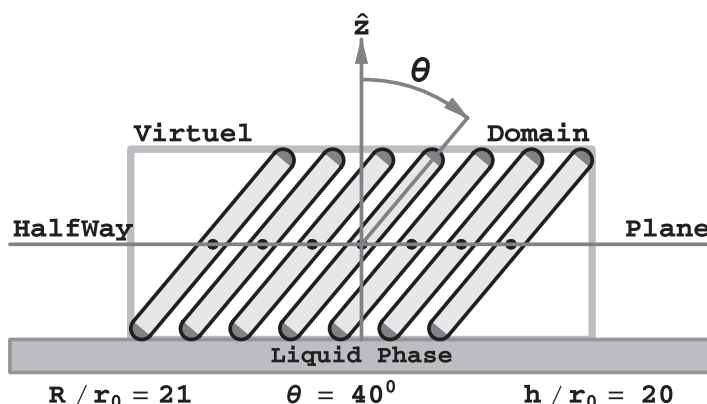
Figure 2. Cross-section of a molecular domain at the liquid–gas interface. The ensemble of parallelly oriented molecules forms the "physical" domain. The physical domain is tilted by an angle θ to the normal to the interface. The circumscribing cylinder forms the "virtual" domain. The axis of the virtual domain is always normal to the interface. Its height is $H(\theta) = 2r_0 + h\cos\theta$. The half-way plane is parallel to the interface and situated half way in-between the base and top of the virtual domain.

The *"virtual domain"* is a right circular cylinder enveloping the molecules of the "physical domain" as shown in figure 2. The axis of this circumscribing cylinder is perpendicular to the liquid–gas interface. Its radius R and height H are determined by the condition that R and H be as small as possible. The height H depends on the inclination of the molecules relative to the interface, and is given by

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

The radius R is equal to half the largest dimension of the projection of the "physical domain" on the interface.

The plane perpendicular to the symmetry axis of the virtual domain and situated half-way in-between the base and the top is referred to as the *half-way plane* (see figure 2). The cross section of the virtual domain in the half-way plane is a disc of radius R. The symmetry axis of the virtual domain passes through the center of this disc. The projection of the physical domain on the half-way plane possesses reflection symmetry through this center. This reflection symmetry is unique to the half-way plane, and is the main reason for choosing to work in it rather than in the plane of the interface [2,11].

2.2. Coordinates

The points of intersection of the molecular axes with the half-way plane define a lattice. When the molecules of the physical domain are vertically oriented we refer to this lattice as the *"reference lattice"* (figure 3). The high degree of symmetry in the case of vertically oriented molecules simplifies the process of introducing and defining a *system of axes* as well as establishing the geometry of the optimal packing. In the case
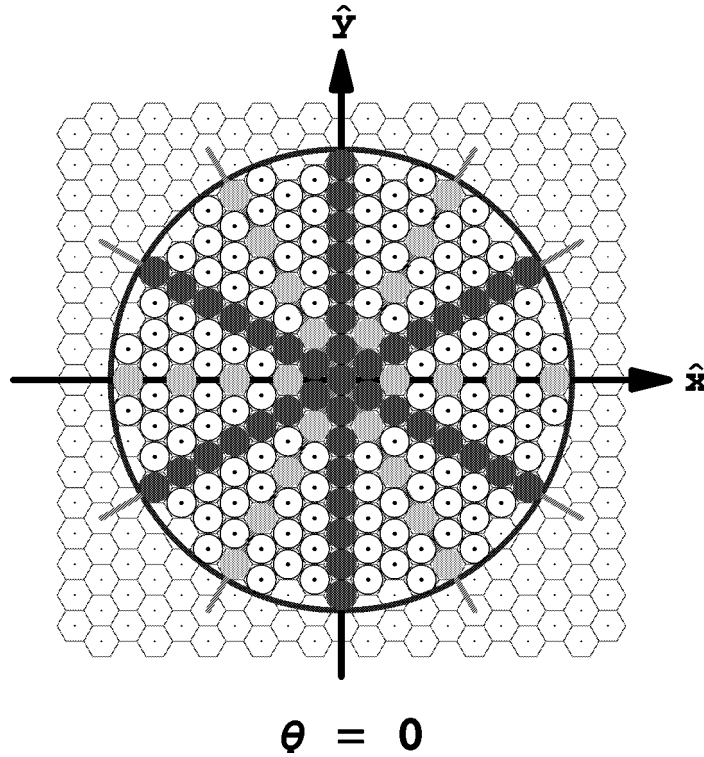
Figure 3. The reference lattice in the half-way plane is formed by the intersection with this plane of the molecular axes when the molecules of the domain are hexagonaly packed and vertically oriented ($\theta = 0$). The $\widehat{x}$ axis coincides with a secondary axis of symmetry of the lattice. The $\widehat{y}$ axis coincides with a primary axis of symmetry of the lattice. Due to hexagonal symmetry, the $\widehat{x}$ and $\widehat{y}$ axes are orthogonal.

of vertically oriented molecules, the optimal packing of spherocylindrical (rod-like) molecules in a cylindrical domain is hexagonal [11], and consequently the reference lattice has three principal and three secondary axes of symmetry as shown in figure 3. Using these symmetry axes we introduce a coordinate system as follows: (i) the $\widehat{z}$ *axis* coincides with the axis of the circumscribing cylinder, that is with the normal to the interface; (ii) the intersection of the $\widehat{z}$ axis with the half-way plane defines the *origin* of coordinates; (iii) the *xy plane* coincides with the half-way plane; (iv) the $\widehat{x}$ *axis* coincides with one of the secondary axes of symmetry; (v) the $\widehat{y}$ *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.

The above defined $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system is fixed to the half-way plane. As the molecules are tilted the half-way plane moves relative to the interface and this $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system moves with it. We also introduce a second coordinate system fixed to the half-way plane. This is the $(\widehat{m}, \widehat{n}, \widehat{z})$ coordinate system shown in figure 4. The $(\widehat{m}, \widehat{n}, \widehat{z})$ coordinate system is obtained from the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate
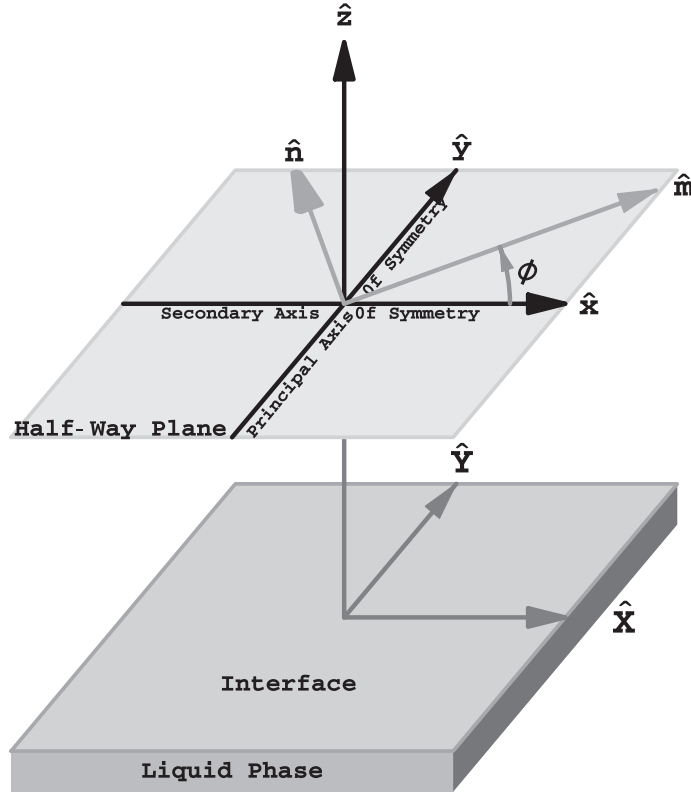
Figure 4. The three systems of coordinates. The $\widehat{x}$ and $\widehat{y}$ axes are as defined in figure 3. The $\widehat{z}$ axis is perpendicular to the interface. The $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system is fixed to the half-way plane. The $(\widehat{m}, \widehat{n}, \widehat{z})$ coordinate system is obtained from the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system by a rotation of angle ϕ about the $\widehat{z}$ axis. The $(\widehat{X}, \widehat{Y}, \widehat{Z})$ coordinate system is "fixed in space". Its origin is on the interface. Its axes are parallel to the $(\widehat{x}, \widehat{y}, \widehat{z})$ axes. Its $\widehat{Z}$ axis coincides with the $\widehat{z}$ axis.

system by a rotation ϕ about the $\widehat{z}$ axis. Hence,

$$\begin{pmatrix} \widehat{m} \\ \widehat{n} \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} \hat{i} \\ \hat{j} \end{pmatrix}, \tag{3}$$

where $\hat{i}$ and $\hat{j}$ are unit vectors along $\widehat{x}$ and $\widehat{y}$, respectively.

In addition to the two above coordinate systems attached to the half-way plane, it is convenient to introduce a space-fixed coordinate system $(\widehat{X}, \widehat{Y}, \widehat{Z})$ as shown in figure 4. The coordinate system $(\widehat{X}, \widehat{Y}, \widehat{Z})$ has its origin on the interface, its $\widehat{Z}$ axis coinciding with $\widehat{z}$ axis, and its $\widehat{X}$ and $\widehat{Y}$ axes parallel to $\widehat{x}$ and $\widehat{y}$, respectively. Hence these two coordinate systems are related by the vertical translation

$$\vec{R} = \vec{r} + \left(r_0 + \frac{h}{2} \cos\theta \right) \widehat{z}. \tag{4}$$

2.3. Dynamic characteristics

The hydrophobic–hydrophilic interaction in-between the molecules of the domain and the liquid phase tends to force the molecules to slide as they tilt in order to stay anchored to the interface. On the other hand, the van der Waals forces that bind the molecules of the domain together, tend to restrict this sliding motion. The ratio of the strength of the restraining van der Waals forces to the driving hydrophobic–hydrophilic forces depends on the length of the aliphatic chain of the molecules and on the angle of inclination of the molecules relative to the normal to the interface.

The restraining effect of the van der Waals forces as the molecules tilt and slide arises from the interaction between the extremities of neighboring atoms and as such is a residual boundary effect. So the relative strength of the restraining effect of the van der Waals forces is roughly proportional to the ratio of the regions of no-contact to the regions of contact between nearest neighbor molecules. For small (realistic) angles of inclination, and phospholipids of biological interest (see table 1 of [2]), this ratio is rather small, and the above assumption is fairly accurate.

We refer to the dominance of the hydrophobic–hydrophilic interaction over the residual van der Waals interaction as *hydro-dominance*. The dynamic characteristics of the Langmuir film model we use here essentially embody this condition.

3. The tilting operation

The phospholipidic molecules of a domain tilt in unison. It is precisely this collective, uniform and unified tilting action that characterizes the domain. The tilting process is subject to the constraint that the polar heads of the molecules remain encored to the interface. This is a consequence of the combined effect of the hydrophilic attraction between the polar heads and the liquid phase, on the one hand, and the hydrophobic repulsion between the aliphatic chain and the liquid phase, on the other hand. The constraint that the polar heads remain anchored to the interface during the process of tilting, forces a realignment of the centers of the molecules on a plane parallel to the interface. We refer to this hydrophobic–hydrophilic constraint as the *hydro-driven realignment*. This realignment is accomplished by sliding the molecules along each other either obliquely up or obliquely down until their polar heads are on the interface.

This continuous complex tilting operation, when examined infinitesimally, can be decomposed into a sequence of three simple consecutive infinitesimal operations that are mutually commutative [5,13]. This commutativity allows us to integrate the infinitesimal parts of each operation separately into one finite operation, and consequently to artificially decompose the finite tilting operation into the following three finite operations (see figure 5):

(i) a global rotation of the physical domain by an angle θ about the $\widehat{n}$ axis, while holding the origin of the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system fixed at a height $H(0)/2 = r_0 + h/2$ above the interface;
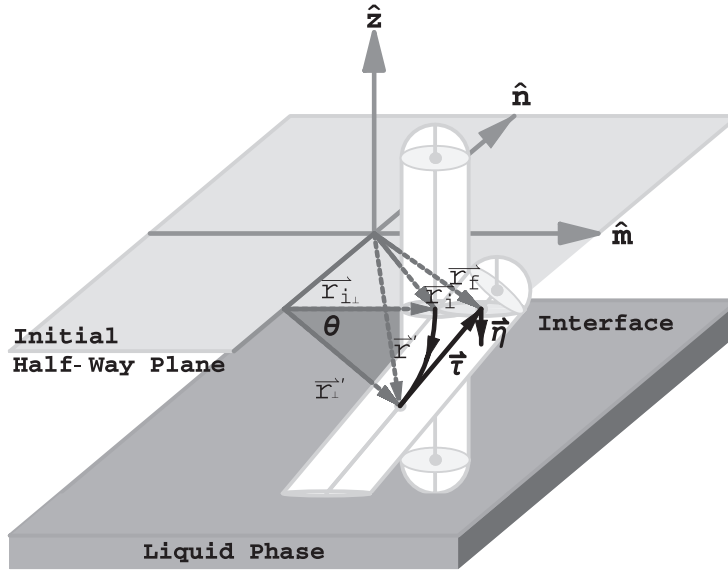
Figure 5. Overall view of the tilting operation as it is artificially decomposed into three finite separate operations: (i) a global rotation of the physical domain by angle θ about the $\widehat{n}$ axis in order to tilt the domain; (ii) a local oblique translation $\vec{\tau} = (\vec{r}'_\perp \times \widehat{n})\tan\theta$ of the individual molecules in order to realign their center on the initial half-way plane; and (iii) a global vertical translation $\vec{\eta} = [h(\cos\theta - 1)/2]\widehat{Z}$ of the physical domain in order to bring down the half-way plane to its final position. The solid black lines map out the path followed by the center of the typical molecule shown.

(ii) a local individual realignment (sliding) of the molecules in order to replace their centers on the half-way plane; and

(iii) a global vertical displacement of the physical domain by a distance $[H(0) - H(\theta)]/2 = h(1 - \cos\theta)/2$.

The first operation (the global rotation) inclines the molecules relative to the interface; the second operation (the local individual realignment) places the polar heads in a plane parallel to the interface; and the third operation (the global vertical displacement) brings down the polar heads to the level of the interface. In this section we will study these three operations in detail. But first we need to establish the notation.

3.1. Notation

In what follows we assume that the domain is tilted by an angle θ in the $\widehat{m}$ direction. Since the $\widehat{m}$ axis makes an angle ϕ with the $\widehat{x}$ axis, then the tilting operator can be characterized by the two angles (θ, ϕ). We refer to this situation as tilting by angle θ in the ϕ (or $\widehat{m}$) direction.

The centers of the molecules (lattice sites) in the half-way plane (the xy plane) are located by the radius vector $\vec{r}$ relative to the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system (with its origin in the half-way plane), and by the radius vector $\vec{R}$ relative to the $(\widehat{X}, \widehat{Y}, \widehat{Z})$

coordinate system (with its origin on the interface). The indices i and f refer to the initial and final positions of the radius vectors respectively, and primes refer to intermediate positions. Thus $\vec{R}_i$ and $\vec{r}_i$ represent the initial position of the center of a molecule when the domain is in its vertical (reference) position ($\theta = 0$); $\vec{R}'$ and $\vec{r}'$ represent the center of the molecule under consideration after the first operation (global rotation); $\vec{R}''$ and $\vec{r}''$ represent the center of the molecule after the second operation (local oblique translation); $\vec{R}_f$ and $\vec{r}_f$ represent the final position of the center of a tilted molecule after the third operation (global vertical translation).

3.2. Generator of infinitesimal rotations

In developing the expression for the tilting operator, we will use the formalism of [1]. Specifically, the generator of infinitesimal rotations about the $\widehat{n}$ axis is given by

$$\boldsymbol{\sigma}_{\hat{n}} = \widehat{n}\times, \tag{5a}$$

where $\widehat{n}$ is a unit vector. The generator $\boldsymbol{\sigma}_{\hat{n}}$ is a null operator for the $\widehat{n}$ axis:

$$\boldsymbol{\sigma}_{\hat{n}}\widehat{n} = 0, \tag{5b}$$

and its odd and even powers are given, respectively, by

$$(\boldsymbol{\sigma}_{\hat{n}})^{2k+1} = (-1)^k \boldsymbol{\sigma}_{\hat{n}}, \quad k = 0, 1, 2, 3, \ldots, \tag{5c}$$

and

$$(\boldsymbol{\sigma}_{\hat{n}})^{2k+2} = (-1)^k \boldsymbol{\sigma}_{\hat{n}}^2, \quad k = 0, 1, 2, 3, \ldots. \tag{5d}$$

The projection operators parallel and perpendicular to the $\widehat{n}$ axis are given by

$$\boldsymbol{P}_{\hat{n}}^{\parallel} = \widehat{n}\widehat{n}\bullet = \boldsymbol{I} + \boldsymbol{\sigma}_{\hat{n}}^2 \quad \text{and} \quad \boldsymbol{P}_{\hat{n}}^{\perp} = \boldsymbol{I} - \widehat{n}\widehat{n}\bullet = -\boldsymbol{\sigma}_{\hat{n}}^2. \tag{5e}$$

The expansion of the generator $\boldsymbol{\sigma}_{\hat{n}}$ in the triplet of basis generators $(\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z)$ about an orthonormal basis $(\widehat{x}, \widehat{y}, \widehat{z})$ is given by

$$\boldsymbol{\sigma}_{\hat{n}} = n_x \boldsymbol{\sigma}_x + n_y \boldsymbol{\sigma}_y + n_z \boldsymbol{\sigma}_z, \tag{5f}$$

and, finally, the rotation operator for a finite rotation by an angle θ about the $\widehat{n}$ axis is given, in terms of the generator $\boldsymbol{\sigma}_{\hat{n}}$, by

$$\boldsymbol{O}_{\hat{n}}(\theta) = \boldsymbol{I} + (\sin\theta)\boldsymbol{\sigma}_{\hat{n}} + (1 - \cos\theta)\boldsymbol{\sigma}_{\hat{n}}^2. \tag{6a}$$

Due to equations (5a) and (5e) this can be alternatively written as

$$\boldsymbol{O}_{\hat{n}}(\theta) = (\cos\theta)\boldsymbol{I} + (\sin\theta)\widehat{n}\times + (1 - \cos\theta)\widehat{n}\widehat{n}\bullet. \tag{6b}$$
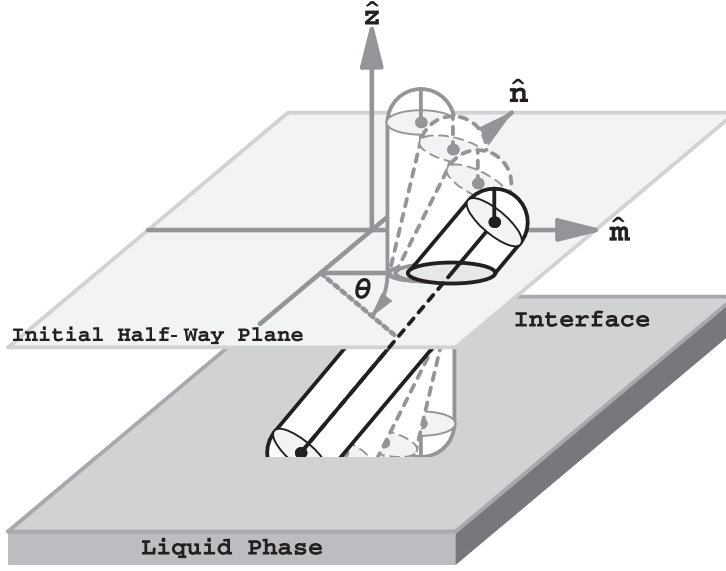
Figure 6. Global rotation of the physical domain by angle θ about the $\widehat{n}$ axis in order to tilt the domain.

3.3. The global rotation

The first operation in the process of tilting the domain by an angle θ in the $\widehat{m}$ direction is a rotation of the whole domain by an angle θ about the $\widehat{n}$ axis, holding the origin of the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system at the fixed height $Z_i = H(0)/2 = r_0 + h/2$ above the interface (see figure 6). This last constraint needs to be clarified. It should be remembered that we have artificially decomposed the complex continuos operation of tilting into three simple operations. The two pathways are identical for infinitesimal operations and give identical final results for finite operations. On the other hand, the intermediate steps in the decomposed finite operations do not lead to realistic situations. Thus even though the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system is actually attached to the half-way plane, and even though the half-way plane drops relative to the interface as the tilting proceeds, we nonetheless temporarily hold the half-way plane (and with it the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system) at a fixed height above the interface until the finite global rotation is completed and then (in the third operation) drop the half-way plane the total required distance in one shot.

Let $\vec{r}\,'$ be the radius vector (relative to the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system) locating the centers of the molecules after the rotation. Then, due to equation (6), $\vec{r}\,'$ is given by

$$\vec{r}\,' = \boldsymbol{O}_{\hat{n}}(\theta)\vec{r}_i = \left[\boldsymbol{I} + (\sin\theta)\boldsymbol{\sigma}_{\hat{n}} + (1 - \cos\theta)\boldsymbol{\sigma}_{\hat{n}}^2\right]\vec{r}_i, \tag{7}$$

where $\vec{r}_i$ is the radius vector (relative to $(\widehat{x}, \widehat{y}, \widehat{z})$) scanning the initial positions (before rotation) of the lattice sites in the half-way plane. We decompose the vector $\vec{r}\,'$ into

components parallel and perpendicular to the rotation axis $\widehat{n}$:

$$\vec{r}' = \vec{r}'_{\parallel} + \vec{r}'_{\perp}. \tag{8}$$

Due to equation (5e), we have

$$\vec{r}'_{\parallel} = \boldsymbol{P}^{\parallel}_{\hat{n}}\vec{r}' = \widehat{n}\big(\widehat{n} \bullet \vec{r}'\big) = \big(\boldsymbol{I} + \boldsymbol{\sigma}^2_{\hat{n}}\big)\vec{r}' \tag{9a}$$

and

$$\vec{r}'_{\perp} = \boldsymbol{P}^{\perp}_{\hat{n}}\vec{r}' = (\boldsymbol{I} - \widehat{n}\widehat{n}\bullet)\vec{r}' = -\boldsymbol{\sigma}^2_{\hat{n}}\vec{r}'. \tag{9b}$$

Combining equations (7), (9a) and (9b), and making use of identities (5c) and (5d) we obtain after some algebra

$$\vec{r}'_{\parallel} = \big(\boldsymbol{I} + \boldsymbol{\sigma}^2_{\hat{n}}\big)\vec{r}_i \tag{10a}$$

and

$$\vec{r}'_{\perp} = \big(\sin\theta\boldsymbol{\sigma}_{\hat{n}} - \cos\theta\boldsymbol{\sigma}^2_{\hat{n}}\big)\vec{r}_i. \tag{10b}$$

3.4. The local oblique realignment

The local oblique realignment of the individual molecules is shown in figure 7, and its parameters have already been introduced in figure 5. As easily seen from these figures, the translation vector $\vec{\tau}$ that slides the molecules of the domain along each
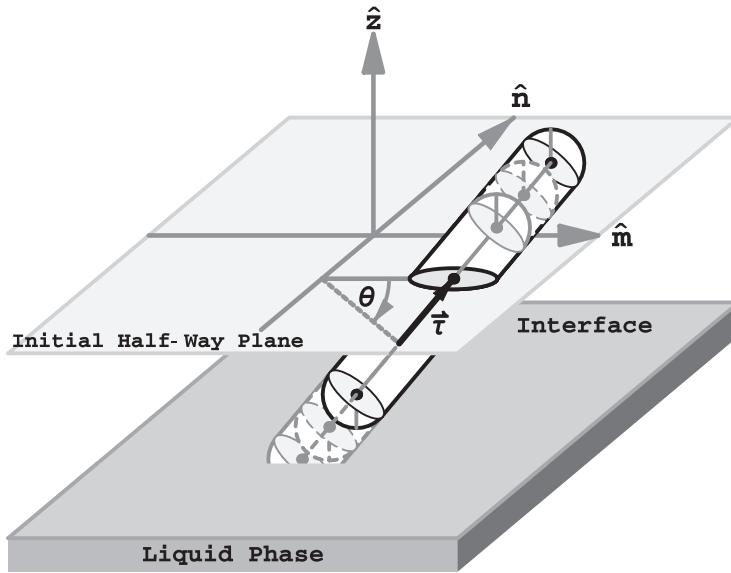

Figure 7. Local oblique translation $\vec{\tau} = (\vec{r}'_{\perp} \times \widehat{n})\tan\theta$ of the individual molecules in order to realign their center on the initial half-way plane.

other is in the direction of $\widehat{r}'_{\perp} \times \widehat{n}$, and if this vector is to replace the centers of the molecules on the initial half-way plane, then its magnitude must be equal to $r'_{\perp} \tan \theta$. Hence,

$$\vec{\tau} = \left(\vec{r}'_{\perp} \times \widehat{n} \right) \tan \theta. \tag{11a}$$

Making use of equations (5a)–(5c) and (8), the above expression for $\vec{\tau}$ reduces to

$$\vec{\tau} = -\boldsymbol{\sigma}_{\widehat{n}} \vec{r}' \tan \theta. \tag{11b}$$

Hence the final position of the centers of the molecules with respect to the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system is given by

$$\vec{r}_f = \vec{r}'' = \vec{r}' + \vec{\tau} = \boldsymbol{T}_{\widehat{n}}(\theta) \vec{r}', \tag{12}$$

where the local realignment operator $\boldsymbol{T}_{\widehat{n}}(\theta)$ is given by

$$\boldsymbol{T}_{\widehat{n}}(\theta) = \boldsymbol{I} - \tan \theta \, \boldsymbol{\sigma}_{\widehat{n}} = \boldsymbol{I} - \tan \theta \widehat{n} \times. \tag{13}$$

Combining equations (7) and (12) we obtain the relation between the initial and final positions of the lattice cites as

$$\vec{r}_f = \boldsymbol{T}_{\widehat{n}}(\theta) \boldsymbol{O}_{\widehat{n}}(\theta) \vec{r}_i, \tag{14}$$

where the radius vectors $\vec{r}_i$ and $\vec{r}_f$ are both measured relative to the $(\widehat{x}, \widehat{y}, \widehat{z})$ coordinate system which is attached to the (mobile) half-way plane.

3.5. The global vertical translation

The global rotation of the physical domain by an angle θ reduces the height of the circumscribing cylinder by $h(1 - \cos \theta)$. Consequently, the half-way plane suffers a vertical translation $\vec{\eta} = [h(\cos \theta - 1)/2]\widehat{Z}$ as measured in the "space-fixed" coordinate system $(\widehat{X}, \widehat{Y}, \widehat{Z})$ (which is attached to the interface). This constitutes the third and last operation in the process of tilting (see figure 8).

Let $\vec{R}_f$ be the radius vector (relative to $(\widehat{X}, \widehat{Y}, \widehat{Z})$) locating the final positions of the centers of the molecules after tilting. Since initially, the half way plane is at a height $r_0 + (h/2)$ above the interface, then

$$\vec{R}_f = \left[r_0 + (h/2) \right] \widehat{Z} + \vec{r}_f + \vec{\eta} = \left[r_0 + (h/2) \cos \theta \right] \widehat{Z} + \vec{r}_f, \tag{15a}$$

as expected from equation (4). Making use of equation (14) to express $\vec{r}_f$ in terms of $\vec{r}_i$, and of equation (4) to express $\vec{r}_i$ in terms of $\vec{R}_i$, the above equation can be rewritten as

$$\vec{R}_f = \boldsymbol{T}_{\widehat{n}}(\theta) \boldsymbol{O}_{\widehat{n}}(\theta) \vec{R}_i + (r_0 + h/2) \left[\boldsymbol{I} - \boldsymbol{T}_{\widehat{n}}(\theta) \boldsymbol{O}_{\widehat{n}}(\theta) \right] \widehat{Z} - (h/2)(1 - \cos \theta) \widehat{Z}. \tag{15b}$$

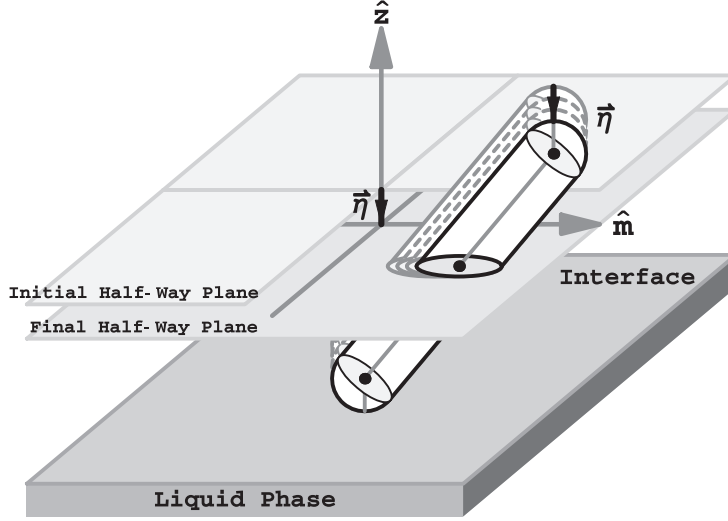This completes the tilting operation.

Figure 8. Global vertical translation $\vec{\eta} = [h(\cos\theta - 1)/2]\widehat{Z}$ of the physical domain in order to bring down the half-way plane to its final position.

4. The tilting operator

4.1. The finite tilting operator

The *tilting operator* $\mathbf{\Lambda}_{\hat{n}}(\theta)$ for molecular domains at the liquid–gas interface is defined by

$$\mathbf{\Lambda}_{\hat{n}}(\theta) = \boldsymbol{T}_{\hat{n}}(\theta)\boldsymbol{O}_{\hat{n}}(\theta), \tag{16}$$

where $\boldsymbol{O}_{\hat{n}}(\theta)$ is the rotation operator defined by equation (6), and $\boldsymbol{T}_{\hat{n}}(\theta)$ is the re-alignment operator defined by equation (13). Substituting for $\boldsymbol{O}_{\hat{n}}(\theta)$ and $\boldsymbol{T}_{\hat{n}}(\theta)$ their expressions as given by equations (6a) and (13), respectively, expanding the resulting expression, making use of equations (5c) and (5d) and of the trigonometric identity $\sec\theta = \cos\theta + \sin\theta\tan\theta$, and simplifying, we obtain (after some algebra) an explicit and very simple expression for the tilting operator $\mathbf{\Lambda}_{\hat{n}}(\theta)$ in the form

$$\mathbf{\Lambda}_{\hat{n}}(\theta) = \boldsymbol{I} + (1 - \sec\theta)\boldsymbol{\sigma}_{\hat{n}}^2. \tag{17a}$$

Making use of equation (5e) this can alternatively be written as

$$\mathbf{\Lambda}_{\hat{n}}(\theta) = \sec\theta\boldsymbol{I} + (1 - \sec\theta)\widehat{n}\widehat{n}\bullet. \tag{17b}$$

From equation (3) we have $\widehat{n} = -\hat{i}\sin\phi + \hat{j}\cos\phi$, and hence the above operator can also be written more explicitly as

$$\mathbf{\Lambda}(\theta, \phi) = \sec\theta\boldsymbol{I} + (1 - \sec\theta)\big[\sin^2\phi\hat{i}\hat{i} - \sin\phi\cos\phi\big(\hat{i}\hat{j} + \hat{j}\hat{i}\big) + \cos^2\phi\hat{j}\hat{j}\big]\bullet. \tag{17c}$$

The matrix elements of the tilting operator in the $(\widehat{x}_1, \widehat{x}_2, \widehat{x}_3) \equiv (\widehat{x}, \widehat{y}, \widehat{z})$ basis are given by

$$\big[\mathbf{\Lambda}_{\hat{n}}(\theta)\big]_{\alpha\beta} = \widehat{x}_\alpha \bullet \mathbf{\Lambda}_{\hat{n}}(\theta)\widehat{x}_\beta = \sec\theta\,\delta_{\alpha\beta} + (1 - \sec\theta)n_\alpha n_\beta. \qquad (17\mathrm{d})$$

Since $(n_1, n_2, n_3) = (-\sin\phi, \cos\phi, 0)$, then substituting for the components of $\widehat{n}$, we obtain the following matrix expression:

$$\mathbf{\Lambda}_{\hat{n}}(\theta) = \sec\theta \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + (1 - \sec\theta) \begin{pmatrix} \sin^2\phi & -\sin\phi\cos\phi & 0 \\ -\sin\phi\cos\phi & \cos^2\phi & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (17\mathrm{e})$$

In terms of the tilting operator, the relations between the initial and final vectors locating the lattice sites can be written succinctly as

$$\vec{r}_f = \mathbf{\Lambda}_{\hat{n}}(\theta)\vec{r}_i \qquad (18\mathrm{a})$$

and

$$\vec{R}_f = \mathbf{\Lambda}_{\hat{n}}(\theta)\vec{R}_i + \big[r_0 + (h/2)\big]\big[\boldsymbol{I} - \mathbf{\Lambda}_{\hat{n}}(\theta)\big]\widehat{Z} - (h/2)(1 - \cos\theta)\widehat{Z}. \qquad (18\mathrm{b})$$

Making use of expression (17b) for the tilting operator, the above equations reduce to

$$\vec{r}_f = (\sec\theta)\vec{r}_i + (1 - \sec\theta)\big(\widehat{n} \bullet \vec{r}_i\big)\widehat{n} \qquad (19\mathrm{a})$$

and

$$\vec{R}_f = (\sec\theta)\vec{R}_i + (1 - \sec\theta)\big(\widehat{n} \bullet \vec{R}_i\big)\widehat{n} - \big[r_0(\sec\theta - 1) + (h/2)\sin\theta\tan\theta\big]\widehat{Z}. \quad (19\mathrm{b})$$

In obtaining (19b) we made use of the fact that $\widehat{n} \bullet \widehat{Z} = 0$, and of the trigonometric identity $\sec\theta - \cos\theta = \sin\theta\tan\theta$.

4.2. The infinitesimal tilting operator

The change in the final lattice due to an infinitesimal change in the angle and direction of inclination can be derived from equation (18a) as

$$\mathrm{d}\vec{r}_f = \big[\mathrm{d}\mathbf{\Lambda}_{\hat{n}}(\theta)\big]\vec{r}_i, \qquad (20)$$

where the *infinitesimal tilting operator* $\mathrm{d}\mathbf{\Lambda}_{\hat{n}}(\theta)$ is given by

$$\mathrm{d}\mathbf{\Lambda}_{\hat{n}}(\theta) = (1 - \sec\theta)\big(\mathrm{d}\boldsymbol{\sigma}_{\hat{n}}^2\big) - \sec\theta\tan\theta\,\mathrm{d}\theta\,\boldsymbol{\sigma}_{\hat{n}}^2, \qquad (21\mathrm{a})$$

or explicitly as

$$\mathrm{d}\mathbf{\Lambda}_{\hat{n}}(\theta) = \sec\theta\tan\theta\,\mathrm{d}\theta\big[\boldsymbol{I} - \widehat{n}\widehat{n}\bullet\big] + (1 - \sec\theta)\big[(\mathrm{d}\widehat{n})\widehat{n}\bullet + \widehat{n}(\mathrm{d}\widehat{n})\bullet\big]. \qquad (21\mathrm{b})$$

Alternatively, in terms of the angle ϕ it is given by

$$\mathrm{d}\mathbf{\Lambda}(\theta, \phi) = \sec\theta\tan\theta\,\mathrm{d}\theta\big\{\boldsymbol{I} - \big[\sin^2\phi\,\widehat{i}\widehat{i} - \sin\phi\cos\phi\big(\widehat{i}\widehat{j} + \widehat{j}\widehat{i}\big) + \cos^2\phi\,\widehat{j}\widehat{j}\big]\bullet\big\}$$
$$+ (1 - \sec\theta)\,\mathrm{d}\phi\big[\sin 2\phi\big(\widehat{i}\widehat{i} - \widehat{j}\widehat{j}\big) - \cos 2\phi\big(\widehat{i}\widehat{j} + \widehat{j}\widehat{i}\big)\big]\bullet. \qquad (21\mathrm{c})$$

In matrix form in the basis $(\widehat{x}_1, \widehat{x}_2, \widehat{x}_3) \equiv (\widehat{x}, \widehat{y}, \widehat{z})$ it is given by

$$d\mathbf{\Lambda}(\theta, \phi) = \sec\theta \tan\theta \, d\theta \begin{pmatrix} \cos^2\phi & -\sin\phi\cos\phi & 0 \\ -\sin\phi\cos\phi & \sin^2\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$+ (1 - \sec\theta) \, d\phi \begin{pmatrix} \sin 2\phi & -\cos 2\phi & 0 \\ -\cos 2\phi & -\sin 2\phi & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{21d}$$

The *infinitesimal tilting operator* is useful or studying small orientational oscillations of the domain about a tilted equilibrium position.

4.3. The finite difference tilting operator

Let $\vec{r}_f(\theta_1, \phi_1)$ and $\vec{r}_f(\theta_2, \phi_2)$ be radius vectors locating the sites of two deformed lattices resulting from tilting the initial lattice by θ_1 in the plane $\phi = \phi_1$ and by θ_2 in the plane $\phi = \phi_2$, respectively. Making use of the expression for the tilting operator it can readily be shown that

$$\vec{r}_f(\theta_2, \phi_2) = \vec{r}_f(\theta_1, \phi_1) + \mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2)\vec{r}_f(0, 0), \tag{22}$$

where $\vec{r}_f(0,0) = \vec{r}_i$ is the radius vector locating the sites of the initial lattice (corresponding to vertically aligned molecules), and $\mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2)$, the *finite difference tilting operator*, is given by

$$\mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2) = (1 - \sec\theta_2)\boldsymbol{\sigma}_{\widehat{n}_2}^2 - (1 - \sec\theta_1)\boldsymbol{\sigma}_{\widehat{n}_1}^2, \tag{23a}$$

or more explicitly,

$$\mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2) = (\sec\theta_2 - \sec\theta_1)\boldsymbol{I} + \left[(1 - \sec\theta_2)\widehat{n}_2\widehat{n}_2 - (1 - \sec\theta_1)\widehat{n}_1\widehat{n}_1\right]\bullet, \tag{23b}$$

or again in terms of ϕ_1 and ϕ_2 as

$$\mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2)$$
$$= (\sec\theta_2 - \sec\theta_1)\boldsymbol{I} + \left[(1 - \sec\theta_2)\sin^2\phi_2 - (1 - \sec\theta_1)\sin^2\phi_1\right]\widehat{i}\widehat{i}\bullet$$
$$+ \left[(1 - \sec\theta_2)\cos^2\phi_2 - (1 - \sec\theta_1)\cos^2\phi_1\right]\widehat{j}\widehat{j}\bullet$$
$$- \left[(1 - \sec\theta_2)\sin\phi_2\cos\phi_2 - (1 - \sec\theta_1)\sin\phi_1\cos\phi_1\right]\left(\widehat{i}\widehat{j} + \widehat{j}\widehat{i}\right)\bullet. \tag{23c}$$

The matrix elements of the finite difference tilting operator in the $(\widehat{x}_1, \widehat{x}_2, \widehat{x}_3) \equiv (\widehat{x}, \widehat{y}, \widehat{z})$ basis are given by

$$\left[\mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2)\right]_{\alpha\beta}$$
$$= \widehat{x}_\alpha \bullet \mathbf{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2)\widehat{x}_\beta$$
$$= (\sec\theta_2 - \sec\theta_1)\delta_{\alpha\beta} + \left[(1 - \sec\theta_2)\widehat{n}_{2\alpha}\widehat{n}_{2\beta} - (1 - \sec\theta_1)\widehat{n}_{1\alpha}\widehat{n}_{1\beta}\right]. \tag{23d}$$

Substituting for the components of $\hat{n}$, we obtain the following matrix expression:

$$\boldsymbol{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2) = (\sec\theta_2 - \sec\theta_1) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$+ (1 - \sec\theta_2) \begin{pmatrix} \sin^2\phi_2 & -\sin\phi_2\cos\phi_2 & 0 \\ -\sin\phi_2\cos\phi_2 & \cos^2\phi_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
$$- (1 - \sec\theta_1) \begin{pmatrix} \sin^2\phi_1 & -\sin\phi_1\cos\phi_1 & 0 \\ -\sin\phi_1\cos\phi_1 & \cos^2\phi_1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (23e)$$

5. The deformed lattice

In this section we will apply the tilting operator to the problem of deformation, due to tilting, of the lattice corresponding to (initially) vertically aligned and hexagonally packed molecules. In the initial state of vertically aligned molecules, the lattice formed by the centers of the molecules in the half-way plane is given, relative to the $(\hat{x}, \hat{y}, \hat{z})$ coordinate system, by (see equation (5a) of [2])

$$\vec{r}_{\ell k}(0, 0) = r_0\left[\hat{i}\ell\sqrt{3} + \hat{j}(2k - \ell)\right], \quad (24)$$

where ℓ and k are integers. The zero in the argument of $r_{\ell k}$ indicates that the above lattice corresponds to the case $(\theta, \phi) = (0, 0)$, that is the case of vertically aligned molecules.

If we now tilt the domain by an angle θ in the ϕ direction (about the $\hat{n}$ axis) the deformed lattice is given by

$$\vec{r}_{\ell k}(\theta, \phi) = \boldsymbol{\Lambda}_{\hat{n}}(\theta)\vec{r}_{\ell k}(0, 0) = r_0\left[(\sec\theta)\boldsymbol{I} + (1 - \sec\theta)\hat{n}\hat{n}\bullet\right]\left[\hat{i}\ell\sqrt{3} + \hat{j}(2k - \ell)\right]. \quad (25)$$

Making use of the fact that $\hat{n} \bullet \hat{z} = 0$, $\hat{n} = n_x\hat{i} + n_y\hat{j}$, and $n_x^2 + n_y^2 = 1$, the above expression reduces to

$$\vec{r}_{\ell k}(\theta, \phi) = \hat{i}r_0\left\{\ell\sqrt{3}\left(n_x^2 + n_y^2\sec\theta\right) + (2k - \ell)(1 - \sec\theta)n_xn_y\right\}$$
$$+ \hat{j}r_0\left\{(2k - \ell)\left(n_x^2\sec\theta + n_y^2\right) + \ell\sqrt{3}(1 - \sec\theta)n_xn_y\right\}. \quad (26a)$$

Alternatively, by making use of equation (3) we can explicitly bring out the dependence on the angle ϕ to obtain

$$\vec{r}_{\ell k}(\theta, \phi) = \hat{i}r_0\left\{\ell\sqrt{3}\left(\sin^2\phi + \sec\theta\cos^2\phi\right) - (2k - \ell)(1 - \sec\theta)\sin\phi\cos\phi\right\}$$
$$+ \hat{j}r_0\left\{(2k - \ell)\left(\sec\theta\sin^2\phi + \cos^2\phi\right) - \ell\sqrt{3}(1 - \sec\theta)\sin\phi\cos\phi\right\}. \quad (26b)$$

Equations (26a) and (26b) give the lattice sites of the deformed lattice due to tilting as a function of the tilting angle θ and the direction of tilting expressed either by the angle ϕ determining the tilting plane, or the unit vector $\hat{n}$ determining the axis of rotation.

For $\phi = 0$ the $\widehat{m}$ axis coincides with the $\widehat{x}$ axis and the $\widehat{n}$ axis coincides with the $\widehat{y}$ axis, and the above expression reduces to

$$\vec{r}_{\ell k}(\theta, 0) = r_0\big\{ \big(\ell\sqrt{3}\sec\theta\big)\hat{i} + (2k - \ell)\hat{j}\big\}, \tag{27}$$

which is the expression obtained in [2]. For $\theta = 0$, equation (26b) is, as expected, independent of ϕ and we recover equation (24), which is the expression obtained in [11], for $\vec{r}_{\ell k}(0, 0) = \vec{r}_{\ell k}(0, \phi)$.

6.   Conclusion

Molecules at the liquid–gas interface group into domains. The molecules in a domain are oriented parallel to each other. The intersection of their axes with the half-way plane forms a lattice. As the molecules are tilted relative to the interface, this lattice is deformed. The tilting operator relates the position of the sites of the deformed lattice to those of the initial lattice formed when the molecules of the domain are vertically oriented.

Using the rotation formalism as developed in [1], we have derived a relatively simple, purely operator, coordinate independent expression for the tilting operator $\boldsymbol{\Lambda}_{\hat{n}}(\theta)$. This expression is given by equation (17a) or equivalently by equation (17b). The result is important for dynamic calculations of inclination dependent collective film characteristics, similar to those performed by Kaganer et al. [7]. In addition to its intrinsic importance, the result obtained here, as well as its derivation, underline the potential of the purely operator formalism of [1].

We also used the expression for the tilting operator to derive three secondary results: (i) expression (21) for the infinitesimal tilting operator $d\boldsymbol{\Lambda}(\theta, \phi)$ that reproduces the infinitesimal deformations in the lattice resulting from an infinitesimal tilt of the domain about the equilibrium position (θ, ϕ); (ii) expression (23) for the finite difference tilting operator $\boldsymbol{\Delta}(\theta_1, \phi_1; \theta_2, \phi_2)$ that relates the lattice sites for two different tilting orientations (θ_1, ϕ_1) and (θ_2, ϕ_2); and (iii) the explicit expression (26) for the radius vector $\vec{r}_{\ell k}(\theta, \phi)$ of the deformed lattice, in the special initial case of hexagonally packed spherocylindrical molecules.

The main physical assumption underlying this work is hydro-dominance – the dominance of the "external" hydrophobic–hydrophilic interactions between the molecules of the domain and the interface, over the residual van der Waals interactions in between the molecules of the domain resulting from boundary effects produced by tilting.

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