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## Liquid Crystals

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# Polar and quadrupolar order in smectic liquid crystals

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In several smectic phases the long molecules are tilted towards the layer planes. The molecules in the layers of smectic C phases have a preferred tilt direction with a  $C_2$  rotation axis perpendicular to the tilt plane. If the molecules have a brick-like shape, a configuration possessing the  $D_{2h}$  symmetry is also possible. For molecules shaped like chevrons or bananas, the existence of a smectic phase with the symmetry  $C_v$  was recently reported. We consider different in-plane configurations of smectics using a geometrical approach based on the 'scaled particle theory'. Varying the geometrical parameters of hard rod particles, a phase diagram for several smectic configurations is predicted. Depending on the particle shape, phases with dipolar order ( $C_2$ ,  $C_v$ ) and quadrupolar order ( $D_{2h}$ ) can be stable.

## 1. Introduction

In the smectic C phase (SmC) long molecules are tilted towards the smectic layers (figure 1). The symmetry of a single layer or an infinite stack of these layers is characterized by a  $C_2$  rotation axis. Recently, the discovery of a non-chiral ferroelectric smectic phase consisting of chevron shaped molecules was reported [1]. In a paper by Cladis and Brand [2] this ferroelectric phase was earlier suggested to exist and called smectic P (SmP). The vector of the spontaneous electric polarization is directed parallel to the two fold rotation

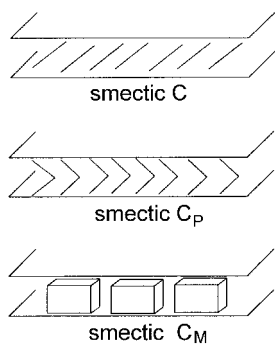


Figure 1. Molecular ordering in the phases C, P and M (after ref. [2]). The symmetries of these phases are  $C_2$ ,  $C_v$  and  $D_{2h}$ , respectively.

axis, which is located in the tilt plane of the molecules. Ferroelectric switching was observed by applying an electric field parallel to the layers [1].

Vectors  $\mathbf{c}$  defined as parallel to the projections of the molecules onto the smectic layer plane would have a preferred direction forming a dipolar order in the phase SmC and SmP. Another order can be achieved by the alignment of molecules possessing a brick-like shape. The aligned bricks form a phase with  $D_{2h}$  symmetry (figure 1). This phase has been called smectic M ([2, 3] and references therein). In figure 1 the smectic C, P and M phases are depicted. While the smectic C and P phases are characterized by a dipolar alignment of the particle projections  $\mathbf{c}$ , the orientational order of the bricks in the smectic M shape is quadrupolar. The smectic M phase could also be formed by tilted or chevron shaped molecules, if the tilt directions  $\mathbf{c}$  and  $-\mathbf{c}$  occur with equal probability.

The ordering in smectic layers is expected to be strongly influenced by molecular shape and the tilt angle. In this paper we compare the stabilities of the smectic in-plane configurations C, P and M using a geometrical approach. For an ensemble of rod-like particles attached to a plane, the free energy is expressed in terms of the density and a distribution function for characterizing the azimuthal particle orientation. Minimizing the free energy, the stable azimuthal configuration is evaluated, while the tilt angle is assumed to be fixed. We investigate

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how the azimuthal distribution depends on the tilt and the particle shape.

Statistical theories for three-dimensional liquid crystals favour the assumption that the molecular repulsion interaction is sufficient to explain the parallel alignment of the long molecules [4–6]. If the density exceeds a critical value, which depends on the length-to-breadth ratio of rod-like particles, the nematic phase defined by a parallel alignment of the molecular long axes is formed. The critical density of the isotropic–nematic phase transition diminishes with increasing length-to-breadth ratio.

In two-dimensional systems, a similar transition is predicted to occur if long particles are lying flat on an isotropic interface [7–9]. Needles oriented randomly at low surface densities form a two-dimensional nematic phase when the density becomes sufficiently high [8]. The particle alignment in the two-dimensional nematic fluid is similar to the order of the bricks in the smectic M phase. If long particles are not horizontally aligned, but tilted away from the interface, an additional orientational ordering is possible. In the nematic state the configurations  $\mathbf{c}$  and  $-\mathbf{c}$  have equal probability (quadrupolar order), whereas this balance is disturbed in the smectic C state. The third phase, the disordered state (D), does not have any dipolar or quadrupolar order. In this state the vector  $\mathbf{c}$  is distributed randomly in all surface directions so that an isotropic two-dimensional fluid results. Because the evaluation of the orientational distribution function turns out to be rather tedious, we also consider a simplified model with only four allowed orientations of the vector  $\mathbf{c}$ . The simplified model provides some qualitative results which are also valid for the model with continuous particle distribution.

Figure 2 demonstrates the geometry of hard particles considered in this paper. The molecule is characterized by three parameters  $a$ ,  $b$  and  $L = l \sin \theta$ , where  $\theta$  defines the molecular tilt with respect to the normal of the smectic layers. The model is also applicable to brick-shaped and chevron-shaped particles. Supposing an ensemble of tilted particles attached to a plane, we investigate the stability of dipolar and quadrupolar order as a function of the geometrical parameters and the surface density. The excluded area effect is investigated by using a mean field approximation in combination with the ‘scaled particle theory’ (see the Appendix), which is known to provide a proper description of systems of hard particles even if the surface density is rather large. The ‘scaled particle theory’ originally developed for hard sphere fluids [10] is also applicable to a fluid of hard cylindrical particles [4,5]. The idea of the theory is to insert a test particle dilated by a factor  $\lambda$  and with a fixed orientation into a particle system. The work  $W(\lambda)$  required to create a hole for the test

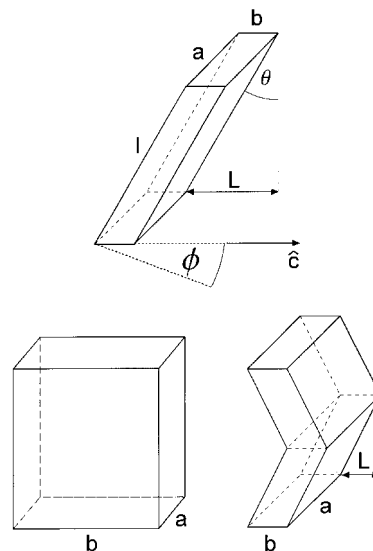


Figure 2. The geometry of the hard rod particles is defined by  $a$ ,  $b$ ,  $l$  and  $L = l \sin \theta$  ( $\theta =$  tilt angle,  $\phi =$  azimuthal angle).

particle is related to the probability  $w(\lambda)$  that this hole is observed due to spontaneous fluctuations. In the limit  $\lambda \rightarrow 1$ , the work  $W(\lambda)$  is connected with the probability  $w$  that the test particle (added to the fluid at an arbitrarily chosen point) does not overlap with any other particles of the system. The contribution  $W(\lambda=1)$ , which is obtained from the probability  $w(\lambda=1)$ , enters into the chemical potential. The recipe for an approximate evaluation of  $w(\lambda=1)$  is used in the Appendix.

## 2. Simplified model with four allowed directions of tilted particles

Some general features of a two-dimensional system of long tilted rods can be explained by considering a simplified model with a reduced number of possible particle orientations. Thus we assume that four azimuthal angles  $\phi_m = m\pi/2$  ( $m = 1-4$ ) for the tilt direction are allowed. It is useful to introduce the dimensionless density  $\psi = Nab/A$ , where  $N$  denotes the number of particles and  $A$  is the area of the two-dimensional system. Assuming that  $N_m$  particles are directed towards the direction  $m$ , the orientational distribution  $\{x\}$  is defined by the fractions  $x_m = N_m/N$  ( $m = 1-4$ ). Obviously, the normalization condition  $x_1 + x_2 + x_3 + x_4 = 1$  is satisfied. For a fixed distribution  $\{x\}$  the free energy of the two-dimensional system is obtained (Appendix) as:

$$\frac{F(T, \{x\}, \psi)}{NkT} = \sum_{i=1}^4 x_i \ln x_i + \ln \psi - \ln(1 - \psi) + \frac{\psi}{1 - \psi} E(\{x\}) + \text{constant} \quad (1)$$

where

$$E(\{x\}) = 1 + 2 \frac{L}{b} (x_1 x_3 + x_2 x_4) + \left( -2 + \frac{a}{b} + \frac{b}{a} + \frac{L}{a} + \frac{L}{b} \right) \times (x_1 x_2 + x_2 x_3 + x_3 x_4 + x_4 x_1).$$

$T$  and  $k$  are the absolute temperature and the Boltzmann constant, respectively. The first and second term on the right hand side of equation (1) correspond to the configuration free energy for an ideal gas mixture consisting of four components. The remaining terms account for the hard-rod interaction which reduces the area available for a particle. Polar and two-dimensional nematic (quadrupolar) order is described by introducing the order parameters  $\eta = x_1 - x_3$  and  $\xi = (x_1 - x_2) + (x_3 - x_4)$ , respectively. Then the fractions  $x_m = N_m/N$  are expressed as

$$x_1 = \frac{1 + \xi + 2\eta}{4}, \quad x_3 = \frac{1 + \xi - 2\eta}{4} \quad \text{and} \quad (2)$$

$$x_2 = x_4 = \frac{1}{4}(1 - \xi).$$

The relations (2) are inserted in the equation for the free energy (1) so that the resulting expression becomes a function of  $\eta$  and  $\xi$ . A stable orientational distribution is accompanied with a minimum of the free energy. Thus we have to satisfy the necessary conditions for a minimum

$$\frac{\partial F}{\partial \eta} = 0 \quad \text{and} \quad \frac{\partial F}{\partial \xi} = 0$$

which can be explicitly written as

$$\ln \left[ \frac{(1 + \xi + 2\eta)(1 + \xi - 2\eta)}{(1 - \xi)^2} \right] = \frac{4\psi(1 - \psi_n)}{\psi_n(1 - \psi)} \xi \quad \text{and}$$

$$\ln \left[ \frac{1 + \xi + 2\eta}{1 + \xi - 2\eta} \right] = \frac{4\psi(1 - \psi_c)}{\psi_c(1 - \psi)} \eta \quad (3)$$

where

$$\psi_n = \frac{2ab}{a^2 + b^2 + Lb} \quad \text{and} \quad \psi_c = \frac{2b}{2b + L}. \quad (4)$$

The equations (3) for the order parameters  $\eta$  and  $\xi$  have three different solutions. The first solution,  $\eta = \xi = 0$ , corresponds to the disordered state (D), which is stable for the density range  $0 < \psi \leq \psi_u$  where  $\psi_u = \min(\psi_c, \psi_n)$ .

If  $\psi > \psi_u$  either the smectic C state with  $\eta \neq 0$  and  $\xi \neq 0$  or the nematic state (N) with  $\eta = 0$  and  $\xi \neq 0$

becomes stable. In the case  $\psi_n < \psi_c$  the phase sequence  $D \rightarrow N \rightarrow \text{SmC}$  is predicted with increasing surface density. The two-dimensional nematic occurs for an intermediate density region. If the density is sufficiently high, the particles are uniformly aligned (SmC order). In the special case  $\theta = 0$ , however, the nematic order cannot transform into the SmC configuration, since the non-tilted particles have a brick-like structure (figure 2). In the opposite case, if  $\psi_n > \psi_c$ , the nematic state is omitted and either the configuration D or SmC is stable depending on the surface density.

Figure 3 shows how the order parameters  $\eta$  and  $\xi$  depend on the density  $\psi$  for three different particle geometries A, B and C, which are given in the figure caption. The upper diagram refers to the case  $\psi_n < \psi_c$ . This condition is satisfied for the parameter sets A and B, whereas the lower diagram (parameters C) is allocated to the case  $\psi_n > \psi_c$ .

In figure 4 the ratio  $L/a$  is plotted versus the ratio  $b/a$ . The upper diagram refers to the model with discrete orientational distribution. Three regions, denoted by I, II and III, are separated by straight lines. For the regions I and II the condition  $\psi_n < \psi_c$  holds so that the phase

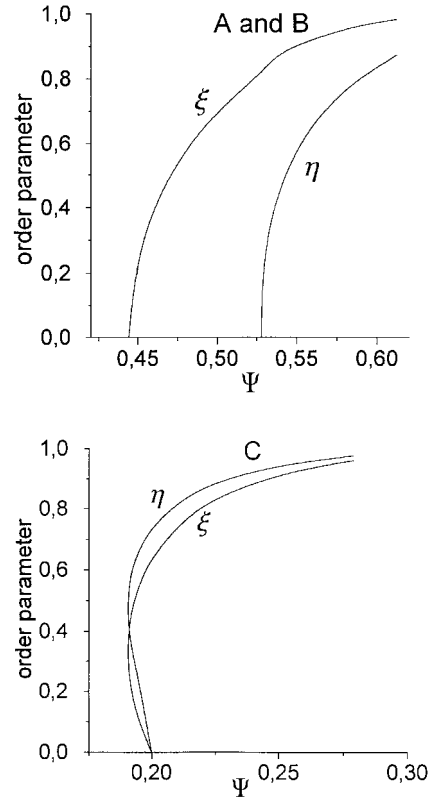


Figure 3. The order parameters  $\xi$  and  $\eta$  for the model with four possible azimuthal orientations are plotted versus the surface density  $\psi$ . Upper diagram: (A)  $L/a = 0.25$  and  $b/a = 0.25$  or (B)  $L/a = 2$  and  $b/a = 2$ . Lower diagram: (C)  $L/a = 2$  and  $b/a = 0.25$ .

sequence  $D \rightarrow N \rightarrow \text{SmC}$  is predicted. In region III only the configurations D and SmC occur ( $\psi_n > \psi_c$ ).

### 3. Hard-rod model with continuous orientational distribution

If the discrete orientational distribution is replaced by a continuous one, the theory is slightly modified. The azimuthal angle  $\phi$  which is enclosed by a fixed axis and the projection  $\epsilon$  of a particle can vary in the interval  $0 \leq \phi < 2\pi$  and the number of particles tilted towards a definite direction is

$$dN = Ng(\phi) d\phi$$

where  $g(\phi)$  denotes the orientational distribution satisfying the normalization condition

$$\int_0^{2\pi} d\phi g(\phi) = 1. \quad (5)$$

Order parameters for the polar and the quadrupolar order are defined by

$$\eta = \int_0^{2\pi} d\phi g(\phi) \cos(\phi) \quad \text{and} \quad \xi = \int_0^{2\pi} d\phi g(\phi) \cos(2\phi). \quad (6)$$

As previously, we can again consider three different configurations D ( $\eta = 0, \xi = 0$ ), N ( $\eta = 0, \xi \neq 0$ ) and SmC ( $\eta \neq 0, \xi \neq 0$ ). Similarly to the discrete model, the free energy is obtained from the 'scaled particle theory' applying a similar procedure to that described in the Appendix. We arrive at the free energy:

$$\begin{aligned} \frac{\hat{F}}{NkT} = & \ln \psi - \ln(1 - \psi) + \int_0^{2\pi} d\phi g(\phi) \ln g(\phi) \\ & + \frac{\psi}{1 - \psi} \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' g(\phi)g(\phi')K(\phi - \phi') \end{aligned} \quad (7)$$

with

$$K(\gamma) = |\cos \gamma| + \frac{a^2 + b^2}{2ab} |\sin \gamma| + \frac{L}{2b} \left( 1 - \cos \gamma + \frac{b}{a} |\sin \gamma| \right)$$

where the notation  $\gamma = \phi - \phi'$  is used. The terms in equation (7) have the same meaning as in equation (1). A stable orientational distribution requires that  $\hat{F}$  is a minimum. This condition leads to the integral equation

$$Cg(\phi) = \exp \left[ -\frac{2\psi}{1 - \psi} \int_0^{2\pi} d\phi' K(\phi - \phi')g(\phi') \right] \quad (8)$$

for the unknown function  $g(\phi)$ . The normalization constant  $C$  is obtained from condition (5). Equation (8) is solvable for small order parameters  $\eta$  and  $\xi$  by using a perturbation method. For densities lower than a critical value the two-dimensional system under consideration

will be isotropic (disordered state D) accompanied with the orientational distribution  $g(\phi) = 1/(2\pi)$ . At higher densities an ordered state is expected to bifurcate from the isotropic state. In this paper we evaluate only the bifurcation point, which can be obtained from the linearized equation (8). Since the integral kernel  $K(\phi - \phi')$  is a periodic function with period  $2\pi$ , the integral

$$K_0 = \frac{1}{2\pi} \int_0^{2\pi} d\phi' K(\phi - \phi')$$

does not depend on  $\phi$ . Inserting the perturbation ansatz

$$g(\phi) = \frac{1}{2\pi} + g_1(\phi) \quad (9)$$

$[\max|g_1(\phi)| \ll 1/(2\pi)]$  into equation (8) and linearizing the result, we obtain

$$\begin{aligned} \hat{C} \left[ \frac{1}{2\pi} + g_1(\phi) \right] = & 1 - \frac{2\psi}{1 - \psi} \int_0^{2\pi} d\phi' \\ & \times [K(\phi - \phi') - K_0]g_1(\phi') \end{aligned}$$

with

$$\hat{C} = C \exp \left( \frac{2\psi}{1 - \psi} K_0 \right).$$

Taking into account expressions (5) and (9) leads to  $\hat{C} = 2\pi$  and thus the linear integral equation

$$g_1(\phi) = -\frac{\psi}{1 - \psi} \frac{1}{\pi} \int_0^{2\pi} d\phi' [K(\phi - \phi') - K_0]g_1(\phi') \quad (10)$$

results. This equation can be solved by expanding the integral kernel to a Fourier series

$$K(\phi - \phi') - K_0 = -\frac{1}{\pi} \sum_{m=1}^{\infty} K_m \cos(\phi - \phi').$$

The first coefficients of the series are:

$$K_1 = \frac{L\pi}{2b}, \quad K_2 = \frac{2(b-a)^2 + Lb}{3ab},$$

$$K_3 = 0 \quad \text{and} \quad K_4 = \frac{2(a+b)^2 + Lb}{15ab}.$$

Inserting the ansatz  $g_1(\phi) = \sum_{n=1}^{\infty} A_n \cos(n\phi)$  into equation (10) leads to the linear equations

$$\left( \pi - \frac{\psi}{1 - \psi} K_n \right) A_n = 0 \quad (\text{for } n = 1, 2, 3, \dots)$$

and thus the set of bifurcation points  $\psi_n = \pi/(\pi + K_n)$  results. Finally, the physically relevant bifurcation point is obtained from the condition  $\psi_u = \min \{ \psi_1, \psi_2, \psi_3, \dots \}$ .

Similarly to the model with discrete orientational distribution, we construct a phase diagram plotting  $L/a$  versus  $b/a$  (figure 4). For small values of  $L/a$  and if  $b \approx a$ , the bifurcation point  $\psi_4$  is the lowest one and thus an orientationally ordered phase with a four-fold rotation axis is predicted to be stable for densities slightly above  $\psi_4$ . But this state is an artefact due to the rectangular corners of the hard rods, and it would disappear if the prismatic particles were replaced by particles with rounded contours. Therefore we only compare the stabilities of the nematic and the smectic C orders. In the lower diagram of figure 4 the three regions I, II and III have the same properties as found for the corresponding regions (upper diagram) of the model with discrete orientational distribution. If  $\psi_1 < \psi_2$  the smectic C order accompanied with the orientational distribution

$$g(\phi) = \frac{1}{2\pi} + \frac{1}{\pi} \eta \cos(\phi) + \dots$$

is stable for  $\psi > \psi_1$ . This condition is satisfied in region III. In the other case, if  $\psi_1 > \psi_2$ , the nematic state

$$g(\phi) = \frac{1}{2\pi} + \frac{1}{\pi} \xi \cos(2\phi) + \dots$$

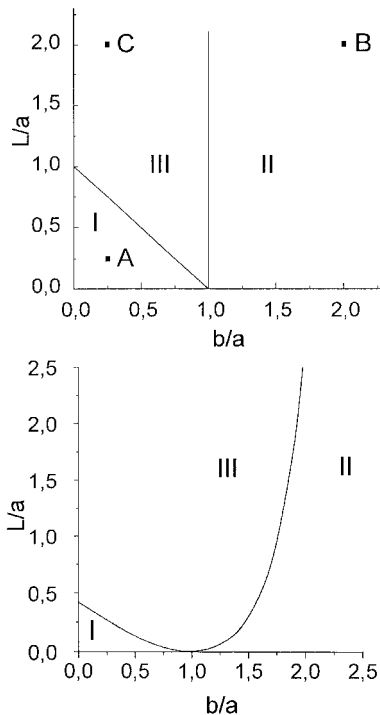


Figure 4. For the phase region III the SmC configuration is the only ordered state, while for the regions I and II the two-dimensional nematic configuration is stable for moderate densities. The upper diagram refers to the model with four possible particle orientations and the lower one to the model with a continuous orientational distribution. The points A, B and C correspond to the set of geometrical parameters  $L/a$  and  $b/a$  given in the caption of figure 3.

emanates from the isotropic state (regions I and II). The order parameters  $\eta$  and  $\xi$  could be explicitly evaluated by taking into account non-linear terms in the perturbation approach for solving equation (8). Similarly to the model with discrete orientational distribution, the nematic state becomes unstable above a second threshold. Above the second threshold the smectic C-like order is predicted to occur if  $L \neq 0$ .

#### 4. Discussion

There are many possible ways to arrange long molecules in two-dimensional fluid and smectic layers of liquid crystals. Using the ‘scaled particle theory’ we have investigated the stability of three configurations for tilted hard rods with different azimuthal order. The stability of a configuration depends on the density, the tilt angle and the shape of the rods. In the smectic C phase only one preferred tilt direction occurs. Introducing a director  $\mathbf{c}$ , which is parallel to the particle projection onto the supporting plane, this order can be considered as dipolar in-plane ordering. It also seems to be possible, however, that a quadrupolar alignment with equal probabilities for the director configurations  $\mathbf{c}$  and  $-\mathbf{c}$  could occur in suitably designed materials. This order appears in a system of long needles lying flat on a surface, if the density is high enough [9]. Brick-like shaped molecules should align also in such a way. We denote this configuration, which can occur on surfaces or in smectic layers, as two-dimensional nematic order.

The nematic order ( $\xi \neq 0$ ,  $\eta = 0$ ) could exist if the cross section of the tilted particles is appropriately elongated. Then the packing entropy, which favours the SmC phase, is compensated by the larger orientational entropy of the nematic configuration. If the density is sufficiently high, however, the nematic configuration must disappear (figure 3), since a dense packing of tilted rods always requires a uniform tilt direction.

Let us apply the geometrical predictions of the hard rod model to the smectic C phase (figure 1). In the conventional smectic C phase, the long molecules rotate rapidly around their long axes [11]. Thus the time-averaged shape of the cross section of a particle should be cylindrical. After tilting a cylinder with diameter  $a$ , the cross section becomes an ellipse with the principal axes  $a$  and  $b = a/\cos \theta$ , where  $\theta$  is the tilt angle. Considering analogously a hard rod with quadratic cross section  $a \times a$ , the tilt produces an elongation parallel to the tilt direction so that  $a \times a/\cos \theta$  is the new cross section. If the tilt angle  $\theta$  is sufficiently high, nematic order should occur for an intermediate density region. According to the lower diagram in figure 3, nematic order is achieved if  $b/a = 1/\cos \theta > 2$ . In this case  $\theta \approx 60^\circ$  is the minimum tilt angle required for observing the nematic configuration. Unfortunately, such a large tilt has

never been observed in smectic phases. If the molecules have a chevron-like shape (as shown in figure 2), however, molecular rotation around the long axis could be prevented. In this case, suitably shaped elongated particles can form a nematic in-plane ordering if the ratio  $b/a$  is sufficiently large.

Finally, it should be noted that amphiphilic molecules adsorbed at the air–water surface are also tilted if the surface density is moderate [12]. Fatty acid monolayers and similar chemical systems do not form a two-dimensional nematic phase. But the nematic alignment of very long phospholipid tubules suspended on the surface of an aqueous solution was recently observed [13].

In conclusion, using a geometrical approach we found that a quadrupolar order in two-dimensional systems and smectic layers could be possible for suitably shaped molecules. In particular, if rotation around the molecular long axes is prevented and the particles are elongated parallel to the tilt direction, the two-dimensional nematic phase is predicted to be stable in an intermediate density region. For sufficiently high densities, however, the nematic order is replaced by the polar (SmC) order, which allows a better packing of tilted particles.

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## Appendix

### Scaled particle approach for a hard-rod fluid

We consider a system of  $N$  differently oriented rod-like molecules grafted on an interface with area  $A$  and suppose that the molecules can be aligned towards  $p$  different directions. The ratio  $x_m = N_m/N$  is the fraction of particles oriented in the direction  $m$  ( $m = 1, 2, \dots, p$ ) and thus the orientational distribution is defined by the set of numbers  $\{x\} = \{x_1, x_2, \dots, x_p\}$ . Differently oriented particles are regarded as distinguishable objects similar to a mixture containing  $p$  components. An arbitrarily chosen area of the surface can be either completely or partially covered by particles or is completely empty. Let  $w_m$  denote the probability that at some arbitrary point of the two-dimensional system a particle with orientation  $m$  ( $m = 1, 2, \dots, p$ ) could be added without overlapping any of the  $N$  hard particles. Then the chemical potential for the component  $m$  of the mixture of oriented particles can be expressed as [6]

$$\beta\mu_m = \ln(N/A) - \ln w_m + C_m(T)$$

where  $\beta = (kT)^{-1}$ . The temperature-dependent term  $C_m(T)$  has the same value for all components and is dropped

in further evaluations. Using the thermodynamic relation

$$F(\rho, T, \{x\}) = N\rho^{-1} \int_0^\rho d\rho' \left[ \sum_{m=1}^p x_m \mu_m(T, \{x\}, \rho') \right]$$

which connects the free energy  $F$  and the chemical potentials of the mixture, we obtain

$$\frac{F(\rho, T, \{x\})}{NkT} = \ln \rho + \sum_{m=1}^p \times x_m \left[ \ln x_m - \rho^{-1} \int_0^\rho d\rho' \ln w_m(\{x\}, \rho') \right]. \quad (\text{A1})$$

Here  $\rho = N/A$  is the surface density. The interface pressure defined by

$$\Pi = \frac{\rho^2}{N} \frac{\partial F}{\partial \rho}$$

is obtained from

$$\beta\Pi = \rho - \int_0^\rho d\rho' \rho' \sum_{m=1}^p x_m \frac{\partial \ln w_m(\{x\}, \rho')}{\partial \rho'}. \quad (\text{A2})$$

For simplicity, we restrict our attention to the model with four allowed orientations (§2). A generalization to an infinite number of orientations ( $p \rightarrow \infty$ ) could be made straightforwardly.

An exact evaluation of the probability  $w_m$  is not possible, but the ‘scaled particle theory’ provides an approximated method which leads to rather good results. The probability that an arbitrarily chosen point of the plane with area  $A$  is not covered by any particle is equal to  $1 - Nab/A$ . It is also possible to obtain the probability  $w_m(\lambda \ll 1)$  that a very small probe (‘scaled particle’) with fixed orientation and the dimensions  $\lambda a$ ,  $\lambda b$  and  $\lambda l$  can be added to the fluid at an arbitrary point without overlapping with other particles. If  $\lambda \ll 1$ , the probability that the probe is in contact with more than one other particle becomes negligibly small. Surrounding all  $N$  particles of the fluid with the scaled particle, we obtain the excluded area into which this small particle cannot enter. The overall excluded area  $A_m^{\text{ex}}$  for a scaled particle with orientation  $m$  ( $m = 1, \dots, 4$ ) can be expressed as

$$\begin{aligned} A_1^{\text{ex}} &= N_1 a_{\uparrow\uparrow} + N_2 a_{\perp} + N_3 a_{\uparrow\downarrow} + N_4 a_{\perp}, \\ A_2^{\text{ex}} &= N_1 a_{\perp} + N_2 a_{\uparrow\uparrow} + N_3 a_{\perp} + N_4 a_{\uparrow\downarrow} \\ A_3^{\text{ex}} &= N_1 a_{\uparrow\downarrow} + N_2 a_{\perp} + N_3 a_{\uparrow\uparrow} + N_4 a_{\perp} \quad \text{and} \\ A_4^{\text{ex}} &= N_1 a_{\perp} + N_2 a_{\uparrow\downarrow} + N_3 a_{\perp} + N_4 a_{\uparrow\uparrow} \end{aligned}$$

where the excluded areas per particle  $a_{\uparrow\uparrow}$ ,  $a_{\uparrow\downarrow}$  and  $a_{\perp}$  depend on the mutual orientation of the probe (scaled particle) and the particle of fluid. The orientation can be parallel, antiparallel or perpendicular, respectively.

A geometrical consideration shows that

$$\begin{aligned} a_{\uparrow\uparrow} &= (a + \lambda a)(b + \lambda b) \\ a_{\uparrow 3} &= (b + \lambda b + 2\lambda L)(a + \lambda a) \\ a_{\perp} &= (a + \lambda b)(\lambda a + b) + \lambda L(\lambda + 1)(a + b). \end{aligned}$$

For the antiparallel orientation the excluded area  $a_{\uparrow 3}$  is depicted in figure 5. Then the probability that a small scaled particle with orientation  $m$  can be added to an arbitrary point of the surface without overlapping is

$$\begin{aligned} w_1(\lambda \ll 1) &= 1 - \rho(x_1 a_{\uparrow\uparrow} + x_2 a_{\perp} + x_3 a_{\uparrow 3} + x_4 a_{\perp}) \\ w_2(\lambda \ll 1) &= 1 - \rho(x_1 a_{\perp} + x_2 a_{\uparrow\uparrow} + x_3 a_{\perp} + x_4 a_{\uparrow 3}) \\ w_3(\lambda \ll 1) &= 1 - \rho(x_1 a_{\uparrow 3} + x_2 a_{\perp} + x_3 a_{\uparrow\uparrow} + x_4 a_{\perp}) \\ w_4(\lambda \ll 1) &= 1 - \rho(x_1 a_{\perp} + x_2 a_{\uparrow 3} + x_3 a_{\perp} + x_4 a_{\uparrow\uparrow}). \end{aligned} \quad (\text{A3})$$

The starting point of the ‘scaled particle theory’ is the assumption that the probability  $w_m$  can be approximately obtained from the first terms of a Taylor expansion:

$$\begin{aligned} \ln w_m(\lambda) &= \ln w_m(\lambda=0) + \lambda \left[ \frac{\partial \ln w_m}{\partial \lambda} \right]_{\lambda=0} \\ &+ \frac{\lambda^2}{2} \left[ \frac{\partial^2 \ln w_m}{\partial \lambda^2} \right]_{\lambda=0} + \dots \end{aligned} \quad (\text{A4})$$

Using the relations (A3), we get the first coefficients of the expansion

$$\ln w_i(\lambda=0) = \ln(1 - \rho ab), \quad (\text{A5})$$

$$\begin{aligned} \left( \frac{dw_1}{d\lambda} \right)_{\lambda=0} &= -\rho \{ 2x_1 ab + [a^2 + b^2 + L(a+b)]x_2 \\ &+ 2(ab + La)x_3 + x_4 [a^2 + b^2 + L(a+b)] \} \end{aligned} \quad (\text{A6})$$

The corresponding derivative  $(dw_m/d\lambda)_{\lambda=0}$  for  $m=2, 3$  and  $4$  is obtained by renumbering the indices. The second derivative  $(d^2 \ln w_m/d\lambda^2)_{\lambda=0}$  is evaluated heuristically, considering the grand canonical partition

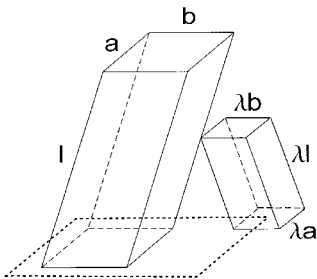


Figure 5. The excluded area  $a_{\uparrow 3}$  is obtained by moving the ‘scaled particle’ around an ‘oppositely tilted’ particle of the fluid.

function  $\Xi$  for a large area ( $\lambda \gg 1$ ). Since  $w_m(\lambda) = 1/\Xi$  ( $i=1, \dots, 4$ ) corresponds to the probability that an arbitrarily chosen area  $\lambda a \times \lambda b$  (which is assumed to be an open thermodynamic system) does not contain any particle [10], the relation

$$\ln w_i(\lambda \gg 1) = 1/\Xi = -\frac{\Pi \lambda^2 ab}{kT} \quad (\text{A7})$$

is satisfied ( $\Pi$ , surface pressure). Therefore we get

$$\left( \frac{d^2 \ln w_i}{d\lambda^2} \right)_{\lambda=0} = -\frac{2ab\Pi}{kT}. \quad (\text{A8})$$

Using equations (A3–8), the sum

$$\sum_{i=1}^4 x_i \ln w_i(\lambda=1) = \ln(1 - \rho ab) - \frac{2\rho ab}{1 - \rho ab} E(\{x\}) - \frac{\Pi ab}{kT} \quad (\text{A9})$$

is evaluated, where

$$\begin{aligned} E(\{x\}) &= 1 + 2 \frac{L}{b} (x_1 x_3 + x_2 x_4) + \left( \frac{a}{b} + \frac{b}{a} - 2 + \frac{L}{a} + \frac{L}{b} \right) \\ &\times (x_1 x_2 + x_2 x_3 + x_3 x_4 + x_4 x_1). \end{aligned}$$

Deriving equation (A9) with respect to  $\rho$  leads to

$$\begin{aligned} \frac{\partial}{\partial \rho} \sum_{i=1}^4 x_i \ln w_i(\lambda=1) &= -\frac{ab}{1 - \rho ab} \\ &- \frac{2ab}{(1 - \rho ab)^2} E(\{x\}) - \frac{ab}{kT} \frac{\partial \Pi}{\partial \rho}. \end{aligned} \quad (\text{A10})$$

On the other hand, differentiating equation (A2) results in

$$\frac{1}{kT} \frac{\partial \Pi}{\partial \rho} = 1 - \rho \frac{\partial}{\partial \rho} \sum_{i=1}^4 x_i \ln w_i(\lambda=1). \quad (\text{A11})$$

Combining equations (A10) and (A11) yields

$$\frac{1 - \rho ab}{kT} \frac{\partial \Pi}{\partial \rho} = 1 + \frac{\rho ab}{1 - \rho ab} + \frac{2\rho ab}{(1 - \rho ab)^2} E(\{x\}). \quad (\text{A12})$$

The surface pressure  $\Pi$ , which can be measured for amphiphilic molecules spread at an air–water surface (Langmuir monolayer), results from integration of equation (A12) taking into account  $\Pi(\rho=0) = 0$ . Thus we get

$$\frac{ab}{kT} \Pi = \frac{\psi}{(1 - \psi)^2} \{ 1 + [E(\{x\}) - 1] \psi \} \quad (\text{A13})$$



where  $\psi = \rho ab$ . Finally, combining equations (A1), (A10) and (A12), the free energy can be written as

$$\frac{F(T, \{x\}, \rho)}{NkT} = \sum_{i=1}^4 x_i \ln x_i + \ln \psi - \ln(1 - \psi) + \frac{\psi}{1 - \psi} E(\{x\}) + \text{constant}. \quad (\text{A14})$$

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