Grafted Rods: A Tilting Phase Transition

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Abstract - A tilting phase transition is predicted for systems comprising rod like molecules which are irreversibly grafted to a flat surface, so that the non interacting rods are perpendicularly oriented. The transition is controlled by the grafting density $\rho$. It occurs as $\rho$ increases as a result of the interplay between two energies. Tilt is favoured by the van-der-Waals attraction between the rods. It is opposed by the bending elasticity of the grafting functionality. The role of temperature is discussed, and the tilting mechanism is compared to other tilting transitions reported in the literature.

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1 Introduction

Anisotropic molecules forming thermotropic and lyotropic liquid crystals can exhibit tilt. The onset of tilt is the characteristic of the smectic A-smectic C phase transition[1]. Tilted phases are observed in monolayers formed by amphiphilic molecules[2]. A variety of tilting phase transitions are possible at solid-fluid interfaces incorporating anisotropic molecules[3]-[7]. Diverse molecular mechanisms can give rise to such phase transitions. In the following, we propose a novel mechanism for the development of tilt at surfaces carrying grafted rods. In particular, we consider a flat solid surface supporting covalently bound rodlike molecules at a surface density $\rho < 1$. The rods are grafted to the surface so that isolated rods are oriented along the surface normal. The grafting functionality, the “joint”, is assumed to allow bending at the price of an elastic energy penalty. A tilting phase transition is predicted to occur as the grafting density $\rho$ increases. The tilt is favoured by the van-der-Waals attraction between the rods, but is opposed by the bending penalty. The interplay between these two energies gives rise to a tilting phase transition. The transition is predicted at zero temperature. However, the mechanism still works at sufficiently low finite temperatures, as we shall argue in the discussion.

From a fundamental perspective, this mechanism is of interest as a complement to the variety of tilting mechanisms studied in the literature. Tilting transitions are also of importance for the design of alignment layers for liquid crystal displays[8]. The orientation of the nematic director inside a liquid crystal cell with no electric or magnetic field applied is usually determined by the interface. Properly designed interfaces supply the desired in-plane asymmetry as well as a certain ”pretilt” angle. Grafted liquid crystal (LC) layers
may form good alignment layers, when the LC-director adopts the tilt of the
grafted layer. In practice, the tilt of the nematic director may not be equal
to the tilt of the grafted layer due to the complicated interaction between the
nematic medium and the layer. This does not however detract from the prac-
tical potential of this system. A tilting phase transition driven by the grafting
density may provide a scheme to fabricate alignment layers with an arbitrary
tilt angle.

Another aspect of grafted layers of interest to liquid crystal align-ment is
their behavior under nematic orientational stress. Such stresses occur during
the Frederiks transition and are of high practical importance as well. Coupling
between the tilting phase transition and the Frederiks transition is expected
to reduce the switching voltage of such devices.[3]

There are a number of reports, where rods have been covalently attached
to a surface.[9, 10, 11]. In most cases, however, the joint is assumed to be
so flexible that it will not show any resistance to bending. Recently, attach-
ment with rigid joints has been claimed as well.[12, 13]. Note however, that
a rigid joint does not necessarily imply perpendicular orientation. The angle
of the joint will depend on details of the chemistry. Right-angled joints are
the exception rather than the rule. If, however, the tilt angle is small and the
in-plane direction of tilt is random, it is reasonable to describe the rods as
perpendicularly oriented.

The essential physics involved is discussed in section II for a highly simpli-
ced case: A linear array of grafted rods. An analysis of the two dimensional case
is presented in section III. A comparison to previously discussed tilting phase
transitions is given in the discussion.

3
2 The Linear Array

The underlying physics of the tilting transition are most easily understood in the case of a linear array. The rods, of length $L$ and diameter $a$, are grafted onto a straight line at regular intervals of width $D$. In the absence of rod-rod interactions, the grafting functionality imposes perpendicular orientation of the rods, i.e. the angle between the rods and the surface normal is $\gamma = 0$. However, the joint can be deformed with a bending elastic penalty of

$$U_{\text{bend}} = \sum_{i=1}^{\infty} A_i \sin^{2i} \gamma, \quad (1)$$

where $A_i$ are non negative phenomenological constants specified in units of energy. The rods also experience mutual van-der-Waals attraction. We picture the rods as comprising monomers of size $a[14]$. The non retarded van-der-Waals attraction between two monomers separated by a distance $r$ is

$$w = -c/r^6, \quad (2)$$

where $c$ is a material constant with units of $[\text{energy}]\cdot[\text{length}]^6$. The van-der-Waals attraction between two parallel rods, $E(D, \gamma)$, may be obtained by integration of the pairwise interactions between monomers belonging to the different rods (see Appendix A). At $D/L < 1$, the leading terms in $E(D, \gamma)$ are

$$E(D, \gamma) = -\frac{K}{(d \cos \gamma)^5} \left\{ \frac{3\pi}{2} + d \cos \gamma (\cos^2 \gamma - 3 - 3 \gamma \tan \gamma) + O(d^5) \right\} \quad (3)$$

with $d = D/L$ and $K = c/(4a^2L^4)$. Note that $E(D, \gamma)$ favors large tilts since in this limit the reduced distance between the rods is $D \cos \gamma < D$. Notice further that $E(D, \gamma)$ diverges at $\gamma = \pi/2$, when the rods are fully tilted. This last feature is however an artefact, since $\gamma = \pi/2$ is actually unattainable
because of excluded volume interactions between the rods. An upper bound for the maximal possible tilt in the $D/L < 1$ case is $\gamma_{up} = \arccos(a/D)$.

To analyze the phase behaviour, it is convenient to consider $E(D, \gamma)$ in the limit of $d \ll 1$ and $\gamma \ll 1$. In this limit, where corrections due to the finite length of the rods are negligible, the leading terms in the expansion of $E(D, \gamma)$ in powers of $\sin^2 \gamma$ are

$$E(D, \gamma) = -(3\pi K/2d^5)[1 + (5/2)\sin^2 \gamma + (35/8)\sin^4 \gamma + \cdots] = -\sum_{i=1}^{\infty} B_i \sin^{2i} \gamma.$$  \hspace{1cm} (4)

We now consider the total van-der-Waals energy, $U_{vdW}$, of a rod in a uniformly tilted array. To obtain $U_{vdW}$ we sum the pairwise interactions of the rod i.e. $U_{vdW} = 2 \sum_{n=1}^{\infty} E(nD, \gamma)$. In the limit of $D/L \ll 1$, when all terms in $E(D, \gamma)$ exhibit a $D^{-5}$ dependence, the result is

$$U_{vdW} = 2\zeta(5)E(D, \gamma),$$  \hspace{1cm} (5)

where $\zeta(5) = \sum_{i=1}^{\infty} k^{-5} \approx 1.037$ is the appropriate Riemann zeta function. In doing so, we assume that the van der Waals interactions are additive. That is the case when the dielectric susceptibility of the materials is an additive function of the constituting components i.e. when the susceptibility is proportional to the concentration of the rods\[15\]. One should however note that this requirement in not always fulfilled\[16\]. If one considers as an approximation only nearest neighbour interactions, the calculated interaction energy $U_{vdW} = 2E(D, \gamma)$ is very close to (5). Hence the total van der Waals energy is dominated by the nearest neighbour contributions.

The behaviour of the linear array of rods is determined by the total energy per rod $U = U_{\text{bend}} + U_{vdW}$. It is instructive to consider the behaviour of $U$ in
a number of scenarios. If one overlooks the excluded volume effect between the rods, $U_{vdW}$ diverges at $\gamma = \pi/2$. When $U_{bend}$ is finite at $\gamma = \pi/2$, this divergence dominates the behaviour of $U$, $U(\gamma = \pi/2) = -\infty$, indicating that all the rods are tilted. While $U(\gamma)$ may exhibit two minima, $U(\pi/2) = -\infty$ always corresponds to the equilibrium state in this scenario. A richer repertoire is possible when the bending penalty at $\gamma = \pi/2$ is infinite as well. In that case, all terms in the expansion of $U_{bend}$ have to be retained. Consider, for example, the situation when the coefficients of $\sin^{2i}\gamma$ of $U_{bend}$ and $U_{vdW}$ are such that $A_i - B_i > 0$ for all $i \geq 2$. A second order tilting phase transition is expected when $A_1 - B_1 = 0$ i.e. $A_1/K = 15\pi/4d^5$ with $d = D/L$ or $d = d_c = (15\pi K/4A_1)^{1/5}$. The rods are perpendicular to the surface, $\gamma = 0$, when $d > d_c$, while for $d < d_c$ they are tilted at angle of $\gamma \propto \sqrt{d_c - d}$. A first order phase transition is expected at $A_1 - B_1 > 0$, if some of the higher order terms are negative and large enough such that $\sum_{i \geq 2} (A_i - B_i) \sin^{2i}\gamma < 0$ for some value of $\gamma < \gamma_{up}$.

The role of higher order terms of $U_{bend}$ is certainly important. A discussion based on this effect suffers however from two disadvantages. Typically, the higher order $A_i$’s are unknown. Also, a chemical design allowing for control of these parameters is impractical. To simplify the analysis, we assume that the bending energy is Hookean up to a cutoff angle $\gamma_{up}$. For specificity, we assume that it is the result of excluded volume interactions and hence given by $\gamma_{up} = \arccos(a/D)$ as noted earlier. Note however $\gamma_{up}$ may also be imposed by the bending potential.

It is helpful to consider first $U$ in the limit of $d \ll 1$ and $\gamma \ll 1$, retaining only the first order terms of $U_{vdW}$ and $U_{bend}$ as specified by (1) and (4). $U$ is
then given by

\[ U = [A_1 - 15\pi K\zeta(5)/2d^5]\sin^2\gamma. \]  \hspace{1cm} (6)

When \( \epsilon = A_1 - 15\pi K\zeta(5)/2d^5 > 0 \), the system may exhibit a first order tilting phase transition. We shall discuss this scenario in greater detail shortly. A second order transition is expected when \( \epsilon = 0 \), while if \( \epsilon < 0 \) the system will be tilted. To analyze the first order transition, it is helpful to express \( U \) in terms of (1) and (3). The energy per rod in the limit of \( d \ll 1 \) is then

\[ U = A_1\sin^2\gamma - \alpha/(d^5\cos^5\gamma), \]  \hspace{1cm} (7)

where \( \alpha = 3\pi\zeta(5)K \) and \( \gamma \) is allowed to vary between 0 and \( \gamma_{up} \). \( U \) is minimal at \( \gamma = 0 \), where \( U(0) = -\alpha/d^5 \), and at \( \gamma_{up} \), where \( U(\gamma_{up}) = A_1\sin^2\gamma_{up} - \alpha/(d^5\cos^5\gamma_{up}) \). It is maximal at \( 0 < \gamma_{max} < \gamma_{up} \), defined by \( \cos^7\gamma_{max} = 5\alpha/2A_1d^5 \). A first order phase transition between an untilted phase and a phase tilted at an angle \( \gamma_{up} \) occurs when \( U(0) = U(\gamma_{up}) \) or \( \alpha/d^5A_1 = \sin^2\gamma_{up}/(\cos^{-5}\gamma_{up} - 1) \).

3 The Planar Case

To extend our considerations to two dimensional, planar arrays, it is necessary to allow for two geometrical effects. First, for a given rod the number of interacting neighbors increases with the distance. Thus, a shell of radius \( r \) and thickness \( dr \) contains \( \rho r dr \) interacting rods, while in the linear array the number is always \( \rho dr \). Second, in the two dimensional case the shortest distance between parallel rods, \( \delta \), varies with azimuthal angle, \( \phi \), between the vector joining the grafting sites and the direction of the tilt. When \( \phi = 0 \) the shortest distance is \( \delta = r\cos\gamma \) while for \( \phi = \pi/2 \) it is \( \delta = r \). In general, \( \delta \) is
given by $\delta = r(1 - \cos^2 \phi \sin^2 \gamma)^{1/2}$ (Figure 1). In realistic situations, it is also necessary to allow for the randomness of the grafting sites. These are unlikely to form a regular lattice. It is thus useful to characterize the array of grafting sites by a pair distribution function

$$g(r) = \rho h(r).$$

(8)

The introduction of $g(r)$ also simplifies the mathematical treatment of the problem. The van-der-Waals interaction energy per rod in a uniformly tilted array is

$$U_{vdW} = \rho \int_0^\infty r dr \int_0^{2\pi} d\phi h(r) V(r, \phi, \gamma),$$

(9)

where $V(r, \phi, \gamma) = E(r, \theta)$ and $\theta$ is defined by $\sin \theta = \sin \gamma \cos \phi$. It is then possible to specify $U_{vdW}$ in terms of the inverse moments of $h(r)$

$$\mu_3 = \int_0^L h(r) dr / r^3 \quad \mu_4 = \int_0^L h(r) dr / r^4,$$

(10)

leading to

$$U_{vdW}(\rho, \gamma) = -\frac{\rho c \pi}{a^2} \mu_3 [2F_1 \left( \frac{1}{2}, \frac{5}{2}, 1, \sin^2 \gamma \right) \frac{\pi}{2} l - \frac{1}{\cos^4 \gamma}] + R(\gamma)$$

(11)

with the hypergeometric function $2F_1(1/2, 5/2, \sin^2 \gamma) = \int_0^{\pi/2} d\phi [1 - \sin^2 \gamma \cos^2 \phi]^{-5/2}$ and $l = L(3 \mu_4)/(2 \mu_3)$. The remainder $R$ is of order $1/L^2$ (see Appendix B).

For simplicity, we take $h(r)$ to be a simple step function

$$h(r) = \Theta(r - D)$$

(12)

with the minimal distance between rods $D$. At $D \ll L$, the inverse moments $\mu_i$ are then given by $\mu_i = 1/((i - 1)D^{i-1})$ and $l = L/D$. We further assume that the minimal distance between rods depends on the grafting density according to a proportionality law $\rho = \nu / D^2$. This implies that the rod grafting sites are
distribute evenly on the plane, like in the case of the linear array discussed in section 2, where the distance between rods is kept fixed. The van-der-Waals energy can then again be expanded in powers of \( \sin \gamma \).

\[
U_{vdW}(\rho, \gamma) = -\bar{K}L\sqrt{\rho^5}\{1+(5/4)\sin^2 \gamma+(105/64)\sin^4 \gamma+\cdots\} = -\sum_i \bar{B}_i \sin^{2i} \gamma
\]

(13)

with \( \bar{K} = c\pi/(4a^2\sqrt{\rho^5}) \). After combining this expression with the bending energy per rod (1), one can follow the discussion from the previous section: A second order transition is expected at \( A_1 = \bar{B}_1 \), i.e. at the critical density

\[
\rho = \rho_c = (\frac{4A_1}{5\bar{K}})^{2/5} \cdot L^{-2/5}.
\]

(14)

It may be preempted at some lower density by a first order tilt transition, if the cutoff angle \( \gamma_{up} \) is large enough such that \( U_{vdW}(\rho_c, \gamma_{up}) - U_{vdW}(\rho_c, 0) + U_{bend}(\gamma_{up}) = 0 \).

The van der Waals energy in the limit \( D/L \ll 1 \) scales like \( L\sqrt{\rho^5} \), whereas the bending energy per rod is independent of rod length and grafting density. Hence the densities, at which phase transitions occur, scale with the rod length \( L \) as \( \rho_c \propto L^{-2/5} \).

We note that these considerations only hold under the supposition that the rods are distributed evenly on the plane, \( D \propto 1/\sqrt{\rho} \), as mentioned above. If the rods are grafted independently of each other, a Poisson distribution is expected. In this case, the assumption \( D = a \) with the monomer size \( a \) may be more appropriate. Eqn (13) then has to be replaced by

\[
U_{vdW}(\rho, \gamma) = -\frac{c\pi}{4a^5}\rho L\{1+(5/4)\sin^2 \gamma+(105/64)\sin^4 \gamma+\cdots\}
\]

(15)

and densities of phase transitions scale with the rod length as \( \rho_c \propto 1/L \). A second order phase transition is expected at \( \rho_c = (16a^5A_1)/(5\pi cL) \). However, in this case, the validity of a mean field averaging as performed in eqn (9)
becomes questionable. This is because domains with different tilt order and local defects of the tilt order parameter may become important even at zero temperature.

4 Discussion

The tilting behaviour considered in this paper results from the interplay between three factors: The van-der-Waals attraction between the rods, the bending elasticity of the joint and the grafting constraints. Clearly no joint is perfectly rigid. The necessary grafting constraints involve two ingredients: (i) The bonding of the rods’ ends to a flat surface in a manner imposing perpendicular orientation of the non-interacting rods. (ii) The absence of lateral mobility. The rods start to tilt at the minimal grafting density $\rho_c$, where the effect of the attractive interaction starts to overcome the bending penalty. Upon further increasing the grafting density, the excluded volume interactions between rods gain importance. As the rods are pushed together, they gradually stand up and finally undergo another continuous transition to an untilted state at $a = D$, where $\gamma_{up} = \arccos(a/D) = 0$. This second transition is driven by the interplay between attractive and repulsive interaction. Thus one expects tilt order in a well-defined density regime (Figure 2).

We should note that, at zero temperature, there is no entropic opposition to the in plane symmetry breaking associated with collective tilt. At finite temperatures, however, the entropy comes into play, giving rise to a variety of new phenomena:

First, it is well known that Goldstone excitations will destroy any true long range order in two dimensional systems with continuous symmetry, where the
ground state is continuously degenerated \[^{17}\]. In our case, the Goldstone modes are long wavelength fluctuations of the in plane tilt direction. At sufficiently low temperatures, however, one still has quasi long range order, \(i.e\). the correlation functions decay algebraically. Unless preempted by a first order transition, Kosterlitz-Thouless-type unbinding of vortex excitations is expected to destroy this order at high temperatures. Note that the energy contained in the vortices will approach zero as the tilt goes to zero. Therefore systems with a small tilt will undergo a Kosterlitz-Thouless transition at lower temperatures than systems with high tilt. This implies that the tilting phase behaviour at finite, sufficiently low, temperatures is very similar to the zero temperature behaviour – but with two differences: (i) the tilted state now has quasi long range order rather than true long range order, and (ii) the second order tilting transitions are replaced by Kosterlitz-Thouless transitions.

Second, the entropy being another factor which opposes collective tilt, it may assume the role of the bending elasticity at finite temperatures. Indeed, the competition of attractive interactions between rods and rod orientational entropy gives rise to a scenario of tilting transitions which is very similar to the one discussed here\[^{5, 6}\]. The details may be different because the entropy will depend on the lateral density due to the packing constraints, whereas the bending elasticity is independent of lateral density.

When lateral mobility is allowed, phase separation will replace the tilting phase transition (cf. \[^{7, 18}\]), because the surface free energy of untilted rods is higher than that of tilted rods. Note however that this last scenario can be modified by several factors. First, if the rods are given some flexibility, the loss of surface free energy per chain upon lowering the chain density is compensated
in part by the gain of conformational entropy. As a consequence, phase separation occurs at lower surface densities. Self consistent field calculations show that, for sufficiently flexible chains, the areal density of the condensed phase may be low enough to favour tilt \[19\]. Second, the phase separated condensed phase may support tilt even in systems of perfectly stiff rods if this is energetically rewarded, e.g. by attractive chain-surface interactions \[5, 20, 21, 22\]. Third, the distance of closest approach between grafting sites may be larger than \(a\), the rod diameter. This last situation is reminiscent of the onset of tilt in amphiphilic monolayers, when the distance between “grafting sites” is determined by the effective radius of the ionic head group \[23\]. A similar mechanism \[4\] for the development of tilt has been proposed for lamellae formed by rod-coil diblock copolymers \(i.e.\) polymers consisting of a rod like block joined to a flexible, coil like block. These can form lamellae in a selective solvent which is a precipitant for the rods. In this case the surface free energy of the close packed rods opposes the tilt which is favoured by the repulsive interactions between the overlapping coils. These last tilt mechanisms are however less closely related to our system since they do not involve rods grafted to a surface with \(\rho < 1\). The rods are always closely packed. Furthermore, the driving force for the tilt comes from units outside the rods (substrate, head groups and flexible blocks respectively) and will not operate in a system consisting solely of rods.

As discussed in the introduction, tilting transitions are particularly important, from a technical point of view, in relation to liquid crystal alignment. If the surface is in contact with a nematic liquid crystal, the tilt of the rods at the surface will influence the director in the bulk of the liquid crystal, and vice
versa. Tilt transitions such as the one discussed here will then translate into “anchoring transitions”, which involve changes of the direction of alignment in the bulk of the liquid crystal.

In this context, it is instructive to briefly discuss the tilting phase transition predicted for liquid crystalline polymers (LCPs) grafted onto a flat surface immersed in a good nematic solvent. In this case the tilt results from the interplay between the repulsive monomer-monomer interactions and the elasticity of the solvent. This situation involves a number of distinct features. First, the effect is expected in the case of long, main chain LCPs supporting a number of hairpin defects. Such LCPs adopt a highly anisotropic, ellipsoidal form such that their major axis is aligned with the nematic director. Second, the effect depends on the anchoring conditions imposed by the grafting surface. It is predicted when the anchoring is homogeneous i.e. the nematic director at the interface is parallel to the surface. As a result of the coupling between the LCPs and the nematic solvent, the orientation of the isolated LCPs is with their major axis parallel to the surface. As the grafting density increases, the overlap between the LCPs grows. This, in turn, results in an increase of the repulsive interactions between the LCPs. These can be weakened by tilting the LCPs thus decreasing the monomer volume fraction within the layer. The onset of tilt is however opposed by the elasticity of the nematic solvent since it results in a distortion of the nematic medium. The interplay of these two contributions gives rise to a second order tilting phase transition. Tilt is now favoured by repulsive interactions rather than by attraction. The role of the joint is assumed by the nematic solvent. The coupling between the LCP and the oriented nematic determines the orientation of the isolated LCPs and gives
rise to the elastic penalty that opposes tilt.

As compared to the case studied in the paper and the tilting transitions discussed so far, the last scenario is different in that the tilting transition does not involve in-plane symmetry breaking. The azimuthal symmetry is already broken in the “untilted” state, in which the LCPs lie parallel to the surface. This is an effect of the nematic medium, which insures collective alignment even at the absence of direct interaction between the molecules. Such tilting transitions without symmetry breaking are frequently found in liquid crystal systems.

An experimental example are anchoring transitions induced by trans-cis isomerizations of azobenzene molecules, which are covalently attached to the surface and immersed in a nematic LC solvent. In these cases, the rods are attached to the surface via flexible spacers comprising 4-10 CH$_2$-units. UV–irradiation induces a transition from a rod like trans conformation to a highly bent cis conformation in the azobenzene molecules. The rods in the trans state favour perpendicular (homeotropic) alignment of the liquid crystal molecules, whereas the substrate and the molecules in the cis state favour parallel (homogeneous) alignment. At a high density of trans units, the competition of these two factors leads to tilted anchoring. UV–irradiation causes the density of trans units to decrease, thereby inducing a continuous transition to an untilted state with parallel anchoring.

5 Conclusions

We have described a tilting transition in grafted layers of rigid rods attached to the surface via a chemical bond, which resists bending. The competition
between bending elasticity on the one hand and van der Waals attraction on the other hand drives the transition. The transition can be of first or second order. We find perpendicular alignment for low coverage, and tilted alignment for higher densities. Second order transitions will be preempted by Kosterlitz-Thouless transitions at nonzero temperatures. We compare the transition with a number of related tilting transitions, which have been discussed in the context of monolayers and of liquid crystal alignment. In some cases similar scenarios are found, where the entropy takes the role of the stiff chemical bond.

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Appendix A: The one dimensional case

We consider two parallel rods of length $L$ grafted at distance $D$ from each other, and uniformly tilted by an angle $\gamma$. The sum of van der Waals interactions between monomers from different rods is then given by

$$E(D, \gamma) = -(c/a^2) \int_0^L dx \int_0^L dx' \frac{1}{[(D \cos \gamma)^2 + (x - x' + D \sin \gamma)^2]^3}. \quad (16)$$

We can decompose the integral and rewrite $E(D, \gamma)$ as $E = -c/(4a^2L) \cdot \hat{E}(D/L, \gamma)$ with

$$\hat{E}(d, \gamma) = 8\int_0^1 dx \frac{1 - x}{(\delta^2 + x^2)^3}$$

$$- \int_0^\varepsilon dx (\varepsilon - x) \left[\frac{1}{(\delta^2 + x^2)^3} - \frac{1/2}{(\delta^2 + (1 + x)^2)^3} - \frac{1/2}{(\delta^2 + (1 - x)^2)^3}\right],$$
where $\delta = d \cos \gamma$ and $\varepsilon = d \sin \gamma$. The integrals can be solved exactly, and one obtains
\begin{equation}
\hat{E}(d, \gamma) = \frac{1}{(d \cos \gamma)^4} \left\{ \cos^2 \gamma - 3 \gamma \tan \gamma - \frac{d^2 \cos^2 \gamma (1 + d^2)}{(1 + d^2)^2 - 4d^2 \sin^2 \gamma} \right. \\
+ \left. \frac{3}{2} \left[ \left( \frac{1 + d \sin \gamma}{d \cos \gamma} \right) \arctan \left( \frac{1 + d \sin \gamma}{d \cos \gamma} \right) + \left( \frac{1 - d \sin \gamma}{d \cos \gamma} \right) \arctan \left( \frac{1 - d \sin \gamma}{d \cos \gamma} \right) \right] \right\}. \tag{17}
\end{equation}

This function can be expanded in different ways for the cases $d < 1$ and $d > 1$:

(a) $d < 1$:
\begin{equation}
\hat{E}(d, \gamma) = \frac{1}{(d \cos \gamma)^4} \left\{ \frac{3\pi}{2d \cos \gamma} + \cos^2 \gamma - 3 \gamma \tan \gamma \right\} + R_1(d, \gamma) \tag{18}
\end{equation}
with $R_1(d, \gamma) = 2/5 + d^2(4 - 32/7 \cdot \cos^2 \gamma) + \mathcal{O}(d^4)$

(b) $d > 1$:
\begin{equation}
\hat{E}(d, \gamma) = \frac{4}{d^6} + \frac{1}{d^8}(14 - 16 \cos^2 \gamma) + \mathcal{O}(\frac{1}{d^{10}}) \equiv R_2(d, \gamma) \tag{19}
\end{equation}

**Appendix B: The planar case**

More generally, let the two rods be grafted on the $xy$-plane and uniformly tilted in the $y$-direction. The vector connecting their grafting points can be parametrized as $\vec{r} = r(\cos \phi, \sin \phi, 0)$ and the tilt vector is $(\sin \gamma, 0, \cos \gamma)$. The interaction between the two rods is then $V(r, \phi; \gamma) = E(r, \theta)$ with an effective tilt angle $\theta$ determined by $r \sin \theta = \vec{r} \vec{t}$ (see Figure 2). We now consider an assembly of rods, which are randomly distributed on the plane according to an isotropic pair distribution function $g(r) = \rho h(r)$. The total van der Waals energy per rod, given by eqn (10), can then be calculated explicitly for the leading terms in the expansion (18). Using the identities
\begin{equation}
\int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - z^2}} = \frac{\pi}{2} {}_2F_1(\frac{1}{2}, \frac{5}{2}, 1, \sin^4 \gamma),
\end{equation}

16
with $z = \sin \gamma \cos \phi$, and

$$
\int_0^{\pi/2} d\phi \left[ \frac{3z \arcsin z}{\sqrt{1 - z^2}} + \frac{z^2 + 2}{(1 - z^2)^2} \right] = \frac{\pi}{\cos^4 \theta}
$$

one obtains eqn (11). The order of magnitude of the neglected rest $R$ can be estimated by

$$
\frac{4a^2L^2}{\rho c} R = \int_0^{2\pi} d\phi \left\{ \int_0^1 dx \, x h(xL)R_1(x, \theta) + \int_1^\infty dx \, x h(xL)R_2(x, \theta) \right\}
\leq 2\pi h_{\text{max}} \left\{ \int_0^1 dx \, x \left( \frac{2}{5} + 4x^2 + \cdots \right) + \int_1^\infty dx \, x \left( \frac{4}{x^6} + 14/x^8 + \cdots \right) \right\}
= \mathcal{O}(1),
$$

hence $R$ is of order $1/L^2$.

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Figures

Figure 1: Two parallel rods grafted on the $xy$-plane
Figure 2: A schematic representation of the tilting transitions upon increasing grafting density $\rho$ at low temperatures