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Spherulite phase induction from positive Gaussian curvature in lyotropic lamellar liquid crystals

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Abstract. — The equilibrium properties of spherulite assemblies in lyotropic lamellar phases are studied within both elastic and statistical models. Following previous models, the spherulites are assumed to be stabilized by their positive Gaussian curvature. Our model predicts that the spherulites should adopt a regular crystalline piling if their core energy $E_c$ is much larger than $k_B T$, or a liquid-like piling with large radius fluctuations if $E_c \sim k_B T$. The spherulites develop an internal pressure depending only on temperature. The existence of a maximum in the distribution of spherulite radii gives a practical criterion for checking the Gaussian curvature efficiency.

1. Introduction.

Lyotropic liquid crystals show a rich variety of lamellar phases where the lamellae are similar to biological membranes [1, 2]. For instance, the ternary system CPCI-hexanol-brine [3] exhibits the following sequence of lamellar phases : $L_1$ (isotropic phase of micelles) → lamellar phase with spherulites → $L_\alpha$ (ordinary lamellar phase) → $L_3$ (« sponge » lamellar phase). The « spherulite phase » is quite novel and not yet recognized as a true thermodynamical phase. It consists of a dense packing of spherulites, which are concentric pilings of spherical bilayers of the ordinary lamellar phase [3]. A few years ago it was proposed that the transition from lamellar phase to sponge phase ($L_\alpha \rightarrow L_3$) was driven by a spontaneous tendency of the lamellae to adopt a negative Gaussian curvature, i.e., a saddle shape [4]. The transition would occur at an elastic threshold at which the Gaussian curvature tendency would overcome the ordinary stabilizing elasticity of the lamellar phase. More recently, it was proposed [5, 6] that the spherulites result from an opposite tendency of the bilayers to adopt a positive Gaussian curvature, i.e., a spherical shape, close to the $L_1 \rightarrow L_\alpha$ transition. There exists probably a similar elastic threshold as for the sponge phase transition, at which the spherulites would be individually stable. However, the model of reference [6] assumed that the spherulites, close to but still below the elastic stability threshold, were rather stabilized by the entropy associated with their disorder, following a model already developed for dilute vesicules [7].

In this paper, we revive the idea that the spherulites of lamellar phases are created by a spontaneous tendency of the bilayers to adopt a positive Gaussian curvature. We study the
spherulite equilibrium both above and below the elastic threshold where the spherulites are individually stable. In part 2, we describe a purely elastic model in which the equilibrium size of the spherulites is calculated. Then we estimate the fluctuations within this elastic model to check the importance of entropy. In part 3, we derive from thermodynamics the spherulite pressure. Then, in a one-dimensional (1D) model, we calculate the statistical mechanics of a dense spherulite packing, taking into account both the size and position fluctuations of the spherulites. We derive (in 1D) the entropic contribution to the spherulite pressure, and we calculate the fluctuations of the spherulite radii. Finally, in 3D, we discuss some general features of the spherulite phase, giving for instance the Gibbs distribution of the spherulite radii as a function of their pressure.

2. Elastic model.

The curvature free-energy density of a lamellar phase depends on the lamella principal curvature radii, \( \rho_1 \) and \( \rho_2 \). For symmetric bilayers, the most general form up to second order in the curvatures is [8]:

\[
f_{el} = \frac{1}{2} K \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right)^2 + \bar{K} \frac{1}{\rho_1 \rho_2}
\]

\( K \), always positive, is the standard elastic constant corresponding to the stabilizing elasticity of the lamellar phase and \( \bar{K} \), of arbitrary sign, is the Gaussian curvature constant. \( \bar{K} > 0 \) favors \( \rho_1 \rho_2 < 0 \) which is realized in the \( L_3 \) sponge phase [4], whereas \( \bar{K} < 0 \) favors \( \rho_1 \rho_2 > 0 \) as in the spherulite phase [5, 6]. In the following, we shall assume \( \bar{K} < 0 \) but, as we shall see, this is not sufficient to stabilize a spherulite.

2.1 Isolated Spherulite. — Let us consider a single spherulite of radius \( R \) embedded in the uniform lamellar phase. It consists in a concentric piling of spherical bilayers with a central core and an interface with the surrounding lamellar phase (Fig. 1). We choose as the origin of energies that of the condensed planar lamellar phase. The core energy is a positive constant.

Fig. 1. — Schematic representation of a single spherulite.
$E_c$. The interfacial energy may be written as $4 \pi R^2 \gamma$. The curvature elastic energy of the spherulite is obtained by integrating $f_{el}$ from the core radius $r_c$ up to $R$. With $\rho_1 = \rho_2 = 1/r$, equation (1) yields $f_{el} = (2K + \ddot{K})r^2$. The spherulite curvature energy is then $4 \pi (2K + \ddot{K})(R - r_c)$. The term proportional to $r_c$ simply renormalizes the core energy $E_c$. The curvature energy of the spherulite reduces then to $4 \pi \ddot{K}R$, with

$$\ddot{K} = 2K + \ddot{K}.$$  

(2)

The total energy of the spherulite, sum of the above described terms, is thus

$$w(R) = E_c + 4 \pi \ddot{K}R + 4 \pi \gamma R^2$$  

(3)

Let us discuss in more detail the physical assumptions included in the derivation of this energy. We have completely ignored any lamella dilation as is usual in confocal textures [9]. The core, in a continuous model, is the region where the order of the lamellar phase goes to zero because of the divergence of the lamella curvature. This "melting" occurs classically over a coherence length where curvature and melting energies are comparable. In our case of a first-order transition, this length is of order $a$ (the lamella period) and the core energy $E_c$ is of order $Ka$. At the microscopic level, the core is probably filled by solvent alone, i.e., completely melted. If the core is larger than $a$, it still implies a net melting energy. If it is smaller than $a$, one could think that the core energy vanishes. In fact, the ordering of the first layer will be very perturbed, yielding also a non-zero core energy $E_c$. Finally, the interfacial tension $\gamma$ can be visualized in the following way: if the spherulite radius $R$ compares with $a$, there may exist a pure elastic matching with the neighbouring lamellar phase. It has then been demonstrated that the total elastic energy scales as a surface energy [6]. In the opposite limit of large $R$, an elastic matching is no longer realistic. The layers must be cut at the spherulite surface, which involves a grain boundary energy also proportional to the spherulite surface. We assume that this property remains valid for all $R$, and to simplify, we take $\gamma$ independent of $R$.

For $\ddot{K} < 0$, the spherulite energy $w(R)$ presents a minimum at $R^* = -\ddot{K}/(2 \gamma)$, which is negative for $(2 \pi \ddot{K})^2 > 4 \pi \gamma E_c$. The spherulite appears as the result of an elastic instability of the lamellar phase. In terms of $\ddot{K}$, the spherulite is stable for $\ddot{K} < -2K - (\gamma E_c/\pi)^{1/2}$ In order to write the results in dimensionless form, let us define $\ddot{k} = \ddot{K}/K$ and $\epsilon_c$, $\ell_K$, $\ell_\gamma$ such that

$$\begin{align*}
E_c &= k_B T \epsilon_c \\
K &= k_B T/\ell_K^2 \\
\gamma &= k_B T/\ell_\gamma^2
\end{align*}$$

(4)

The spherulite stability threshold and the equilibrium radius can be expressed as

$$\begin{align*}
\ddot{k}_s &= -\left(\frac{\epsilon_c}{\pi}\right)^{1/2} \frac{\ell_K}{\ell_\gamma} \\
R^* &= -\frac{1}{2} \ddot{k} \ell_\gamma^2 / \ell_K^2
\end{align*}$$

(5)

The threshold spherulite radius is $R^*(\ddot{k}) = \frac{1}{2} (\epsilon_c/\pi)^{1/2} \ell_\gamma$. For the consistence of the model, this quantity must be larger than the core size, itself larger than the lamella thickness.
A reasonable estimate for \( E_c \) is a few \( \kappa \), where \( \kappa = Ka \) is the bidimensional curvature constant [8]. One can find in the literature [10] that for ternary systems \( \kappa \sim k_B T \) and for pure amphiphilic systems \( \kappa \sim 25 k_B T \). One can therefore expect \( \epsilon_c \sim 3 \) for the former system and \( \epsilon_c \sim 60 \) for the latter one. In practice, with \( \epsilon_c = 10 \), \( R^*(\tilde{\kappa}_a) \gg a \) requires \( \tilde{l}_\gamma \gg a \). This condition seems exaggerated for a thermotropic smectic but may be reasonable for a ternary lyotropic smectic: the cosurfactant may heal the bilayers cut at the spherulite boundary and largely reduce the surface energy defining \( \tilde{l}_\gamma \).

2.2 Dense Assembly of Spherulites. — At first sight, one could expect an assembly of spherulites to consist of a dense packing of spherulites, all having the equilibrium size \( R^* \), as previously defined. We show in the following that densely packed spherulites tend to be much smaller.

Let us consider a dense assembly of \( N \) spherulites in a closed volume \( V \). We assume that the lowest energy state of the system will consist in spherulites having all the same radius \( R \). The average density of the filling can be described by a compacity factor \( c \ll 1 \) such that

\[
N = \frac{4}{3} \pi R^3 = cV.
\]

(6)

Densely packed spherulites still present a surface energy. The interstices between spherulites can be filled either by a long-range oriented lamellar phase, or by lamellae locally parallel to the neighbouring spherulites. The former case is identical to that of an isolated spherulite. For the latter case, a distribution of grain boundaries will appear within the planes that are tangent to each pair of spherulites at their contact point. The energy of these grain boundaries scales also as \( R^2 \). To simplify, we keep writing the surface energy as \( 4 \pi R^2 \gamma \) and assume that the spherulites interact only as hard spheres.

The total elastic energy \( W(R) \) of the assembly is then \( W(R) = N w(R) \), which is proportional to \( w(R)/R^3 \). Making use of equation (6), we find

\[
W(R) = 3 cV \left( \frac{E_c}{4 \pi R^3} + \tilde{K} \frac{R}{R^2} + \frac{\gamma}{R} \right).
\]

(7)

The comparison between \( W(R) \) and \( w(R) \) is shown in figure 2. \( W(R) \) has extrema for

![Graph](image)

Fig. 2. — The free-energy density \( W(R)/V \) of a dense spherulite assembly (plain line) and the free-energy density \( w(R)/v^* \) that would result from filling the space with spherulites having their individual equilibrium radius \( R^* \) (dashed line). The volume \( v^* \) is \( \frac{4}{3} \pi R^*^3 c^{-1} \).
\[ \gamma R^2 + 2 \tilde{k} R + \frac{3}{4} \pi^{-1} E_c = 0. \]
The minimum gives the equilibrium radius of the assembly as
\[ R_a = 2 R^* \left( 1 - \sqrt{1 - \frac{3}{4} \frac{\tilde{k}_s^2}{\tilde{k}^2}} \right). \]  
(8)

The assembly stability threshold, defined by the condition \( W(R_a) = 0 \), is still \( \tilde{k}_s \). At the threshold, we have exactly \( R_a = \frac{1}{2} (\varepsilon_c / \pi)^{1/2} \ell_\gamma = R^*(\tilde{k}_s) \), but above the threshold, \( R_a \) is definitely smaller than \( R^* \), as announced earlier (Fig. 3). This decrease of the radius is energetically favoured because the gain associated with the increase in the spherulite density largely overcomes the individual loss per spherulite. In the limit \( |\tilde{k}| \gg |\tilde{k}_s| \), we have
\[ R_a \sim -\frac{3}{8} (\varepsilon_c \ell_\kappa / \pi) \tilde{k}^{-1} \]
Assuming \( \varepsilon_c = 10 \) (cf. discussion in 2.1) and classically \( \ell_\kappa \sim a \), we find that \( R_a \) reaches the bilayer thickness \( a \) for \( \tilde{k} \sim -1 \). This gives the absolute limit of our elastic model.

Within a dense assembly, each spherulite is constrained at a size far from its own equilibrium size by the hard sphere interactions exerted by its neighbours. The resulting elastic forces exchanged between the spherulites (Fig. 4) build then a pressure, the definition of which will be given in section 3.1. The piling optimal compacity is obtained by minimizing \( W(R_a) \) with respect to \( \ell \). Since \( W(R_a) \propto c \), the spherulite equilibrium piling is the crystalline hexagonal piling that maximizes \( c \). Conversely, below threshold, since \( W(R_a) > 0 \), the system will rather minimize \( c \): the spherulites, which are then metastable, will separate in a dilute piling and consequently adopt their individual equilibrium size \( R^* \) (in the absence of attractive forces between spherulites). The extrapolated \( R_a \) variation for \( \tilde{k} / \tilde{k}_s < 1 \) (Fig. 4) is therefore not physical.

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**Fig. 3.** — Comparison between the equilibrium radius \( R_a \) within a dense assembly and the individual spherulite equilibrium radius \( R^* \). Both are displayed versus the relative Gaussian curvature gain. The plain parts of the curves correspond to the physical path.

**Fig. 4.** — Schematic representation of the pressure arising from the repulsive contact forces exerted between the spherulites in a dense assembly.
2.3 Elastic stability diagram. — We now extend our previous analysis by also considering assemblies of spherulites within the isotropic phase ($L_\alpha$). This is justified by the fact that in reference [6] the spherulites appear close to the $L_\alpha \rightarrow L_\alpha$ transition (although no observation of spherulites in the $L_\alpha$ phase was mentioned). Since the $L_\alpha \rightarrow L_\alpha$ transition occurs when the cosurfactant/surfactant ratio $\phi$ increases and reaches $\phi_0$, we shall consider the spherulite stability in the $(\tilde{k}, \phi)$ space.

The spherulites can survive within the isotropic phase as long as their negative elastic energy compensates their positive condensation free-energy $\frac{4}{3} \pi R^3 \Delta f$. In the vicinity of the $L_1 \rightarrow L_\alpha$ first-order transition, the free-energy difference between the planar lamellar phase ($\phi > \phi_0$) and the isotropic phase ($\phi < \phi_0$) can be approximated by $\Delta f \sim A (\phi_0 - \phi)$. In principle, the boundary between the spherulites and the isotropic phase involves a surface energy coefficient $\gamma$, different from $\gamma$. To simplify, we shall make the crude approximation $\gamma_\alpha = \gamma$. The energy of an assembly of spherulites, now within the isotropic phase, is given by

$$W_i(R) = W(R) + cV \Delta f,$$

since $c$ is also the volume fraction of the spherulites. The spherulite equilibrium radius is still $R_\alpha$, since the minimum of $W_i(R)$ is independent of $\Delta f$. The spherulite stability threshold corresponds to $W_i(R_\alpha) = 0$, which is equivalent to $\frac{1}{3} A (\phi - \phi_0) R_\alpha^3 = (4 \pi)^{-1} E_c + \tilde{K} R_\alpha + \gamma R_\alpha^2$. This condition defines a transition line $L_1 \rightarrow S_1$ between the isotropic phase and the crystal of spherulites within the isotropic phase. The $L_1 \rightarrow S_1$ line equation, in the limit $\phi - \phi_0 \ll 1$ in order that the expression of $\Delta f$ remains valid, is given by

$$\phi_0 - \phi \sim 12 \left( \frac{\pi}{\varepsilon c} \right)^{1/2} k_B T A f^3 \gamma \left( \frac{\tilde{k}}{\tilde{k}_c} - 1 \right).$$

The transition line between the spherulites within the isotropic phase ($S_1$) and the spherulites within the lamellar phase ($S_L$) is given by $\phi = \phi_0$ since we assumed $\gamma_\alpha = \gamma$. Finally, the $L_\alpha \rightarrow S_L$ line is given by $\tilde{k} = \tilde{k}_c$, as shown in section 2.2. All the spherulite transitions are first-order since metastable spherulites can survive beyond the stability threshold. The transition lines $L_1 \rightarrow S_1$ and $S_1 \rightarrow S_L$ are naturally limited to the region $\tilde{k} > -1$, beyond which our elastic model no longer holds since $R_\alpha$ compares then with $a$ as shown in section 2.2. These results are summarized in the phase diagram of figure 5.

![Fig. 5. — Elastic stability diagram of the spherulite phases in the $(\tilde{k}, \phi)$ space. $\tilde{k}$ controls the Gaussian curvature and $\phi$ the lamellar ($L_\alpha$) -> isotropic ($L_1$) transition. $S_L$ and $S_1$ are the spherulite phases within the lamellar and the isotropic phase, respectively. If the spherulite entropy was taken into account, the stability domains of the spherulite phases would become larger.](attachment:image.png)
2.4 Estimate of the disorder within the spherulite assembly. — The above discussed model (Sects. 2.2 and 2.3) was purely elastic and naturally yielded a crystal of spherulites. To test its validity, let us evaluate the thermal fluctuations of the spherule positions and radii.

We shall first estimate the position fluctuations. The energy required to create a vacancy within the spherule crystal is \(-w(R_a)\). From equation (3) and the equation yielding (8), we have \(w(R_a) = -2E_c - 4\pi kR_a\). It is easily shown from equation (8) that \(4\pi kR_a = f(\tilde{k}/\tilde{k}_s)E_c\), where \(f(x) = 4x^2(1 - \sqrt{1 - 3/(4x^2)})\). The vacancy creation energy is therefore

\[
w(R_a) = -g(\tilde{k}/\tilde{k}_s)E_c ,
\]

with \(g(x) = 2 - f(x)\). For \(\tilde{k}/\tilde{k}_s \in [1, \infty]\) (in the stability range of the spherulites), we have \(g(\tilde{k}/\tilde{k}_s) \in [0, 1/2]\). Thus, remarkably, \(w(R_a)\) the elastic energy gain per spherule within the assembly always compares with the core energy \(E_c\). This is clearly apparent in figure 2. To estimate the relative density \(x\) of vacancies/spherulites in the regime \(x \ll 1\), we treat the vacancies as a perfect gas. This gives \(x \sim \exp[w(R_a)/kBT] = \exp[-E_c/k_BT]\). It follows that the spherule positional disorder will be large if \(\varepsilon_c \sim 1\).

We now estimate the size fluctuations of the spherulites to check our hypothesis of a common radius within the assembly. Let us consider a spatial variation of the spherule radius \(R(r) = R_a + \delta R(r)\) close to the elastic minimum. In the reciprocal space, \(\delta R(r)\) is represented by its components \(\delta R_q\). As \(q\) approaches \(\lambda = 2\pi/R_a\), the piling does not remain locally hexagonal and gradient terms must be taken into account. The quadratic variation of the system elastic energy can be written as

\[
\delta H = V \sum_q \frac{1}{2} \alpha (1 + q^2 \xi^2) |\delta R_q|^2 ,
\]

where \(\xi\) is the coherence length associated with the gradient terms. For a constant \(\delta R\), we have \(\delta R_q = \delta R \delta q, 0\) and \(\delta F\) reduces to \(V\frac{1}{2} \alpha \delta R^2\). Identification with our elastic model gives \(\alpha = (d^2/dR^2)|_{R_a} (W/V)\). This quantity, easily calculated from equation (7), can be given the form

\[
\alpha = \frac{3c_3}{2\pi} [1 + g(\tilde{k}/\tilde{k}_s)] \frac{E_c}{R_a^5}
\]

(13)

The value of \(\xi\) is difficult to calculate exactly, but it seems reasonable to expect \(\xi \sim R_a\) which is the piling characteristic length. We have verified, in an elastic model with two spherulite sizes, that this assumption is reasonable. The thermal fluctuations of the size modes are given by the equipartition theorem applied to equation (12), i.e., \(\langle |\delta R_q|^2 \rangle = k_BT[V\alpha(1 + q^2 \xi^2)]^{-1}\) The local fluctuation is then classically obtained by summing over all the modes, i.e., here up to the cut-off \(\lambda\) :

\[
\langle \delta R_p^2 (r) \rangle \sim \frac{V}{(2\pi)^3} \int_0^1 4\pi q^2 dq \frac{k_BT}{V\alpha(1 + q^2 \xi^2)}
\]

(14)

With the values \(\xi = R_a\) and \(\lambda = 2\pi/R_a\) already discussed, equation (14) gives \(\langle \delta R_p^2 \rangle \sim (k_BT/(\alpha R_a^5))\) with a proportionality coefficient \(2(2\pi)^{-2}(2\pi - \arctan(2\pi))\) of order unity. From equation (13), we have \(\alpha R_a^5 \sim E_c\), with a coefficient again of order unity
\[
\left( \text{since } 1 + g(\tilde{k}^2) \in \left[ 1, \frac{3}{2} \right] \right).
\]

Finally, the relative size fluctuation is
\[
\frac{\sqrt{\langle \delta R^2 \rangle}}{R_a} \sim \left( \frac{E_c}{k_B T} \right)^{-1/2}
\]

(15)

Thus the radius fluctuations are also expected to be large for \( \varepsilon_c \sim 1 \).

There should be two kinds of systems according to whether \( \varepsilon_c \) is smaller or larger than unity. Since we expect \( \varepsilon_c \sim 3 \) for ternary lyotropic systems and \( \varepsilon_c \sim 60 \) for pure amphiphilic systems (cf. Sect. 2.1), ternary systems should give liquid-like spherulite packing with large size and position fluctuations, whereas pure lyotropic systems should give crystalline spherulite piling (although metastable disordered glassy states are also expected). This prediction is in agreement with the observations of reference [6].


We showed in the last section that an assembly of spherulites within the lamellar phase is subject to large position and size fluctuations if the spherulite core energy \( E_c \) compares with \( k_B T \). In this regime, our elastic model clearly lacks a significant entropic contribution.

To determine the free energy associated with the spherulite disorder, one should study the statistical mechanics of the system by taking into account all the possible sources of disorder. This is a very daunting task. Besides the disorder associated with the spherulite size and position distributions, various other disorder sources are possible: to explore the various radiiuses, the spherulites must aggregate or dissolve additional bilayers. The corresponding disorder is the distribution of the spherulite growth rates (at least each spherulite may grow or recede). More accurately, one could consider the entropy associated with the lines that are the borders of the aggregating bilayers. The momentum of the spherulites could also be taken into account. The latter may be larger when the spherulites evolve in the isotropic phase (cf. Sect. 2.3). Within the lamellar phase, there may also be an entropy associated with the orientations of the interstitial lamellae between the spherulites. The spherulites may not be exactly spherical. It has been shown [5] that some spherulites are in fact conics of second-species [11]. A corresponding elongation distribution could be taken into account. One could also consider the dilatable elastic deformation modes of the spherulites, etc.

Due to this complexity, it seems illusory to calculate exactly the total entropy of the spherulite system. It is however interesting to estimate the contributions associated with the position and size distributions, specially because the size distribution is measurable [6]. In principle, the radii are coupled with the other degrees of freedom mentioned above. In the following we shall assume that we can consider them as decoupled. Before discussing statistical models, let us first define some thermodynamic parameters that will be relevant in what follows.

3.1 Spherulite pressure and chemical potential. — Let a fluctuating assembly of \( N \) spherulites be placed in a closed volume \( V \) at temperature \( T \). To take into account the assembly fluctuations, we must consider the free-energy \( F(T, V, N) \) of the assembly instead of the elastic energy \( W \) defined in section 2.2. The spherulite free-energy, measured from the planar lamellar free-energy, differs from \( W \) by an entropic contribution \( -TS \) associated with the disorder of the spherulites. Since the total number of spherulites is not fixed, \( N \) plays the role of an internal parameter with respect to which \( F \) must be minimized. This equilibrium condition reads

\[
\mu = 0,
\]

(16)
where $\mu = \partial F / \partial N \big|_{T,V}$ is the spherulite chemical potential. Similarly, the spherulite pressure is defined as $P = -\partial F / \partial V \big|_{T,N}$. From the well-known Legendre transformation $G = F + PV = N\mu$, $\mu$ can be expressed as a function of $P$ and $T$ only. Therefore, we have

$$\mu(P, T) = 0 \Rightarrow P = P(T).$$

The equilibrium spherulite pressure depends only on the temperature. This is reminiscent of the black-body, for which the total number of photons is also free. An interesting consequence is that if one reduces the volume of the spherulite system by exerting an additional pressure, the numbers of spherulites will simultaneously decrease to maintain the pressure to its equilibrium value $P(T)$.

In this paragraph we show that the results of the elastic model (Sect. 2.2) can be recovered within this thermodynamical formalism. In the elastic approximation, $F(V, N)$ reduces to $F = Nw(R)$, with $w(R)$ given by equation (3). The chemical potential is then given by $\mu = \partial F / \partial N \big|_{V} = w + N (\partial w / \partial R) (\partial R / \partial N \big|_{V})$, where $\partial R / \partial N \big|_{V}$ is given by equation (6). We obtain $\mu = w - 1/3 R (\partial w / \partial R) \propto d(w/\!R^3) / dR$. Thus, writing $\mu = 0$ is equivalent to minimize $w/\!R^3$ with respect to $R$. This is exactly what was done in section 2.2 and gave $R = R_{a}$. The spherulite elastic pressure is then $P_{e} = - (\partial F / \partial R \big|_{N}) (\partial R / \partial V \big|_{N})$, i.e.,

$$P_{e} = - \frac{c}{N} 4 \pi R_{a}^{2} \frac{\partial (Nw)}{\partial R} \bigg|_{N} = - c \left( \frac{K}{R_{a}^{2}} + 2 \frac{\gamma}{R_{a}} \right).$$

Since $\mu = 0$ is equivalent to $F = -P_{e}V$, the volumic elastic energy of the spherulite assembly is given by $-P_{e}$. We have thus $P_{e} = 0$ at the stability threshold and $P_{e} > 0$ above threshold.

In a fluctuating spherulite assembly, the total pressure has an additional entropic contribution $P_{s}(T)$ that must be determined by statistical mechanics. We may therefore write

$$P(T) = P_{e} + P_{s}(T).$$

Since $\mu = 0$, the spherulite pressure $P(T)$ is now $-F(T)/V$, opposite of the free-energy. At equilibrium, $F(T)$ will always be strictly negative since entropy will always stabilize a non-zero spherulite density (even if the spherulites are unstable and must be considered as defects). Consequently, $P(T)$ will always be strictly positive. Moreover, the stabilizing spherulite entropy will enlarge the $S_{l}$ and $S_{L}$ domains of figure 5.

3.2 STATISTICAL MECHANICS OF A 1D SYSTEM OF SPHERULITES. — To get some insight into the entropic fluctuations, let us study a simplified 1D problem. We consider $N$ spherulites with arbitrary radii, densely packed along a line of length $L$ (Fig. 6). To solve this problem, we impose that the spherulites reside densely packed. This is a reasonable approximation in the regions of the phase diagram where the spherulites are stable.

The microscopic states of the system are uniquely defined by the set of the spherulite radii $\{R_{1}, R_{2}, \ldots, R_{N}\}$, each being equal to an integer number $n_{i}$ of the bilayer spacing

$$L = P \quad 0 \quad L$$

Fig. 6. — Fluctuating 1D assembly of spherulites, in contact with a thermostat at temperature $T$ and a pressure $P$. 


The total length of the assembly is
\[ L = 2 \sum_i R_i. \]  
\[ \text{(20)} \]

If we fix \( L \), we must take into account the fact that the radii are not independent. It is more convenient to let \( L \) fluctuate and fix the value of the conjugated pressure \( P \). We shall use the Gibbs distribution where the system exchanges both energy and volume with a thermostat at temperature \( T = (\beta k_B)^{-1} \) and pressure \( P \). The partition function of this system
\[ Z(T, P, N) = \sum_{\{n_i\}} e^{-\beta \left( \sum_i w(R_i) + PL \right)} \sim \frac{1}{a^N} \int dR_1 \ldots dR_N e^{-\beta \left( \sum_i w(R_i) + PL \right)} \]  
\[ \text{(21)} \]
is in principle a discrete sum over the spherulite number of bilayers. In the limit where the spherulites are statistically large enough, we can replace the discrete sum by an integral in the range \([0, +\infty[\) (also setting the lower limit to zero instead of \( r_c \)). With the definition of \( L \) and the expression of \( w(R_i) \) given by equation (3), we have
\[ \sum_i w(R_i) + PL = \sum_i \left\{ E_c + (4 \pi \tilde{K} + 2 P) R_i + 4 \pi \gamma R_i^2 \right\}. \]  
\[ \text{(22)} \]
The radiiuses being independent, the partition function (21) factorizes to \( Z = z^N \), with
\[ z(T, P) = e^{-\beta E_c + \frac{\beta (2 \pi \tilde{K} + P)^2}{4 \pi \gamma}} \int_0^\infty \frac{e^{-\beta 4 \pi \gamma \left( R + \frac{2 \pi \tilde{K} + P}{4 \pi \gamma} \right)^2}}{a^N} dR = e^{-\beta 4 \pi \gamma \left( R + \frac{2 \pi \tilde{K} + P}{4 \pi \gamma} \right)^2}. \]  
\[ \text{(23)} \]
The integral in equation (23) is Gaussian and can be expressed via the complementary error function \( \text{erfc} \). Since the potential classically associated with \( Z \) is the free-enthalpy \( G = k_B T \ln Z = N \mu \), the spherulite chemical potential is simply \(-k_B T \ln z\):
\[ \mu(T, P) = E_c - \frac{(2 \pi \tilde{K} + P)^2}{4 \pi \gamma} - k_B T \ln \left[ \frac{1}{4 a} \sqrt{\frac{k_B T}{\gamma}} \text{erfc} \left( \frac{2 \pi \tilde{K} + P}{4 \pi \gamma k_B T} \right) \right]. \]  
\[ \text{(24)} \]

Let us compare this expression with the chemical potential of the 1D elastic model: \( N \) compact identical spherulites with radius \( R = L/(2 N) \) have an energy \( W(R) = N w(R) \) given by equation (3). It follows that \( \mu_e = \partial W/\partial N \big|_L = w(R) - R \partial w/\partial R = E_c - 4 \pi \gamma R^2 \) and \( P = - \partial W/\partial L \big|_N = \frac{1}{2} \partial W/\partial R = -2 \pi \tilde{K} - 4 \pi \gamma R \). Combining these two relations gives
\[ \mu_e(P) = E_c - (2 \pi \tilde{K} + P)^2/(4 \pi \gamma) \]  
which coincides with the first two terms of equation (24). Then, from \( \mu_e = 0 \) (cf. Sect. 3.1), we get the equilibrium radius \( R_e^{(1D)} = \sqrt{E_c/(4 \pi \gamma)} \) and the elastic pressure \( P_e^{(1D)} = P(R_e^{(1D)}) = -\sqrt{4 \pi \gamma E_c} - 2 \pi \tilde{K} \). The elastic threshold (defined by \( P_e^{(1D)} = 0 \)) is still \( \tilde{k}_s \) given by equation (5).

The limit \( T \to 0 \) in equation (24) (artificially keeping \( \tilde{K} \) and \( \gamma \) constants) gives \( \mu(T, P) \to \mu_e(P) \). As expected, when \( T \to 0 \) the statistical model coincides with the elastic one.

The equilibrium pressure \( P(T) \) is given by \( \mu(P, T) = 0 \) (cf. Sect. 3.1). This equation gives
\[ 2 \pi \tilde{K} + P \]  
as a function of \( T \) only. The quantity \( 2 \pi \tilde{K} + P \) can be written as \( P_e^{(1D)}(T) - \sqrt{4 \pi \gamma E_c} \) from the expression of \( P_e^{(1D)} \) and equation (19). Defining the reduced
entropic pressure as

$$p_s(T) = \frac{P_s^{(1D)}(T)}{\sqrt{4 \pi \gamma k_B T}},$$

and $\mu_r = \mu / k_B T$, equation (24) can be rewritten adimensionally as

$$\mu_r = 2 \varepsilon_c^{1/2} p_s - p_s^2 - \ln \left[ \frac{\ell_y}{4 a} \text{erfc} \left( p_s - \varepsilon_c^{1/2} \right) \right].$$

The equilibrium equation $\mu_r = 0$ must be solved numerically and gives $p_s = p_s(\varepsilon_c, \ell_y/a)$. Figure 7 shows the entropic pressure $p_s$ versus $\varepsilon_c$ for $\ell_y/a = 20$ at fixed (room) temperature. We chose $\ell_y/a \gg 1$ to make sure that the spherulites be much larger than the bilayer thickness. Consistently with the fluctuations estimated in section 2.4, the entropic pressure $p_s$ vanishes for $\varepsilon_c \gg 1$.

![Fig. 7. Reduced entropic pressure $p_s$ versus the reduced spherulite core energy $\varepsilon_c$ in the 1D model. The dotted curve represents the ratio between the entropic pressure and the elastic pressure $P_s^{(1D)}/P_e^{(1D)}$ for $\tilde{K} = 2 \tilde{k}$. For large values of $\varepsilon_c$, the entropic pressure is negligible compared with the elastic pressure.](image)

The spherulite average radius can be calculated from $\langle R \rangle = \delta \mu / \partial \left(4 \pi \tilde{K} \right)$ taken at $P = P(T)$, or equivalently from $\langle R \rangle = (16 \pi)^{-1/2} \ell_y \partial \mu / \partial p_s$ taken for the equilibrium value of $p_s$. Taking the derivative of equation (26) and making use of $\mu_r = 0$, we obtain

$$\langle R \rangle \left/ R_e^{(1D)} \right. = 1 - \varepsilon_c^{-1/2} \left[ p_s - \frac{\ell_y}{4 \pi^{1/2} a} e^{-\varepsilon_c} \right].$$

Similarly, the average value of the fluctuation $\delta R = R - \langle R \rangle$ can be calculated from $\langle \delta R^2 \rangle = - k_B T \partial^2 \mu / \partial \left(4 \pi \tilde{K} \right)^2 = - (16 \pi)^{-1} \ell_y^2 \partial^2 \mu / \partial p_s^2$. We find

$$\langle \delta R^2 \rangle \left/ R_e^{(1D)^2} \right. = \frac{1}{2 \varepsilon_c} \left( 1 - \frac{R}{a} e^{-\varepsilon_c} \right).$$

Figure 8 shows $\langle R \rangle / R_e^{(1D)} = r$ and $\sqrt{\langle \delta R^2 \rangle / R_e^{(1D)^2}} = \delta r$ versus $\varepsilon_c$, at fixed temperature and again for $\ell_y/a = 20$. Consistently again with section 2.4, we find that the radius fluctuations are very large for $\varepsilon_c \sim 1$ but vanish for $\varepsilon_c \gg 1$, yielding the 1D elastic model described above.
Fig. 8. — Reduced average spherulite radius and radius fluctuations versus the reduced spherulite core energy $\varepsilon_c$ in the 1D model. For large values of $\varepsilon_c$, the elastic model is valid.

With respect to the elastic model, the spherulites are further stabilized due to the entropic pressure. Indeed, the volumic free-energy being equal to $-(P_c^{(1D)} + P_s^{(1D)})$, the spherulites are already stable at the elastic threshold $\tilde{k}_s$ defined by $P_c^{(1D)} = 0$. However, the exact stability threshold cannot be determined within the present model because the initial dense-packing assumption is no more valid close to the threshold. The entropy due to the separation of the spherulites, that we have neglected close to the threshold, will stabilize the spherulites even more. Consequently, $P_c^{(1D)} + P_s^{(1D)} = 0$ defines an indicative threshold $\tilde{k}^\ast$, the absolute value of which is overestimated. Since, $P_c^{(1D)} + P_s^{(1D)} = -\sqrt{4 \pi \gamma E_c - 2 \pi \tilde{K} + P_s^{(1D)}}$, we obtain

$$\tilde{k}^\ast = (1 - \varepsilon_c^{-1/2} p_3) \tilde{k}_s. \quad (29)$$

As an example, for $\varepsilon_c = 1$ and again $\ell_s/a = 20$, we see from figure 7 that $p_3 \sim 1.6$, thus $\tilde{k}^\ast \sim -0.6 \tilde{k}_s$: the spherulites are now stable for $\tilde{k} = 0$. Therefore if $\varepsilon_c \sim 1$, the entropy can stabilize the spherulites in the region $\tilde{K} \approx -2 \tilde{K}$, as proposed in reference [6].

3.3 RADIUS DISTRIBUTION IN A 3D SYSTEM OF SPHERULITES. — The extension to 3D of the above described model yields a liquid of hard spheres with variable radii. Even with the simplifying compacity hypothesis, it is extremely difficult to count all the microscopic states of such a system. We can however make use of our hypothesis that the spherulites interact only as hard spheres, to apply the canonical distribution to the system consisting in one spherulite, « weakly coupled » to the thermostat made of the lamellar phase containing all other spherulites.

Discarding again all other internal modes, we only keep the spherulite radius $R$ as an internal variable. Our system, consisting in a single spherulite with energy $w(R)$ given by equation (3) and volume $V = \frac{4}{3} \pi R^3$, exchanges both energy and volume with the thermostat at temperature $T = (\beta k_B)^{-1}$ and pressure $P$. The probability density $f(R)$ of a configuration with radius $R$ is therefore proportional to $\exp[-\beta (w(R) + PV)]$, i.e.,

$$f(R) \propto \exp \left[-\beta \left( E_c + \frac{4}{3} \pi \tilde{K} R + \frac{4}{3} \pi \gamma R^2 + P \left( T \frac{4}{3} \pi R^3 \right) \right) \right]. \quad (30)$$

Since the thermostat consists in the assembly of surrounding spherulites, its pressure $P$ cannot be chosen independently of the temperature (cf. sect. 3.1). The function
Fig. 9. — Typical spherulite radius distributions in 3D.

\[ P(T) \] is well-defined but unknown. It could be determined only by solving the whole statistical 3D problem. Nevertheless we can make an interesting prediction from the fact that \( P \) is always positive (for obvious stability reasons in Eq. (30) and more generally for the thermodynamical reasons given in Sect. 3.1). Since \( E_c \), \( \gamma \) and \( P \) are all positive, \( w(R) + PV \) has a minimum at \( R_m \neq 0 \) only if \( \bar{K} < 0 \) (Fig. 9). Therefore, \( f(R) \) must have a non-zero maximum if \( \bar{K} < -2K \) and no maximum if \( \bar{K} > -2K \).

3.4 Spherulite Phases and Spherulite Fluctuations. — In section 3.1 we showed that a small but finite spherulite density of entropic origin will indefinitely persist within the \( L_\alpha \) and \( L_\beta \) phases. This will broaden the spherulite transitions (cf. Fig. 5). Within the present models we cannot determine whether the drop in the spherulite pressure when going from the spherulite region to the \( L_\alpha \) or \( L_\beta \) phases will be sharp enough to define a transition. To overcome this difficulty, we propose to call a spherulite phase a spherulite assembly presenting a maximum in the radius distribution (\( \bar{K} < -2K \), cf. Sect. 3.3) and to consider as a spherulite fluctuation within the mother phase a spherulite assembly without maximum (\( \bar{K} > -2K \)). With this definition, the spherulites are elastically stable (or metastable) within the spherulite phase. Experimentally, the spherulites observed in reference [6] showed an absence of maximum in the size distribution. This would indicate that \( \bar{K} > -2K \) and would correspond in our description to spherulite fluctuations close to the \( S_L \) phase. The \( S_L \) phase would then still remain to be observed as well as the \( S_1 \) phase.

4. Conclusion.

In this paper, we investigated whether positive Gaussian curvature can induce stable phases of spherulites. We first discussed a pure elastic model. Above a stability threshold, an isolated spherulite acquires a negative energy due to its positive Gaussian curvature and has a relatively large size, limited only by its surface energy. However, the lamellar phase fills space with much smaller spherulites. The total energy is then lowered due to the rise in spherulite density, which largely compensates the associated energy loss per spherulite. An elastic pressure develops then within the assembly as the spherulites are constrained to a smaller size than the equilibrium by the hard sphere interactions with neighbours. The spherulite density rise is limited by the spherulite positive core energy. It follows that the elastic energy per spherulite within a dense assembly is always comparable to the core energy \( E_c \).

If \( E_c \gg k_B T \), the energy per spherulite of the order of \( E_c \) is much larger than \( k_B T \) and we expect the spherulite assembly to build a compact hexagonal crystal. We propose
as a possible phase sequence, controlled by the Gaussian curvature constant $\bar{K}$ and the phase component concentrations: isotropic ($L_1$)-spherulite crystal within isotropic-spherulite crystal within lamellar-lamellar ($L_{\alpha}$).

If $E_c \sim k_B T$, the spherulite fluctuations are dominant and we expect a spherulite assembly to build a disordered liquid phase with large radius fluctuations. The spherulite pressure acquires an entropic contribution coming from the radius and position exchanges between the spherulites. From thermodynamics, the total spherulite pressure is then a function $P(T)$ of temperature only, strictly positive and opposite to the volumic free-energy. This follows from the fact that the spherulite number is an internal parameter that adjusts to equilibrium. In a 1D model, we have calculated the entropic contribution to the pressure. The entropy stabilizes the spherulite system beyond the elastic threshold. In 3D, we cannot calculate $P(T)$ but the previous ideas remain valid. We predict the characteristics of the radius distribution function of the (unknown) pressure. The existence of a maximum in the spherulite radius distributions gives a practical criterion to determine the sign of the curvature constant combination $2 K - \bar{K}$.

Finally, to distinguish a spherulite phase from spherulite fluctuations within the mother phase, we proposed the criterion of the existence of a non-zero maximum in the spherulite radius distribution. This « elastic » criterion overcomes the difficulty that the spherulite entropy broadens the spherulite transitions when $E_c \sim k_B T$. If $E_c \gg k_B T$, the spherulites should build a 3D crystal. This is reminiscent of other 3D ordered phases in lyotropics, between isotropic and lamellar phases [2]. In the case where the interstices between the spherulites show long-range smectic order, the system should be considered as an eutectic of the spherulite crystal and the ordinary lamellar phase. For $E_c \sim k_B T$, the fluctuating spherulites form an isotropic liquid phase, which is different from the $L_1$ phase. If the interstices between the spherulites still show long-range smectic order, this spherulite packing then forms a lamellar phase different from the ordinary $L_{\alpha}$ phase. It would be interesting to check the existence of these phases by diffraction experiments. As for the predicted $R(P)$ distribution for one spherulite, it could be checked by micromechanical measurements. The spherulite assemblies described up to now [6] seem to correspond to strong $S_L$ fluctuations in the $L_{\alpha}$ phase and not to the $S_\alpha$ phase itself. Finally, note that our model probably does not apply to multivesicular spherulites [12, 13], in which the additional entropy associated with the shape fluctuation may be dominant.

References