Swelling Kinetics of Layered Structures: Triblock Copolymer Mesogels

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Abstract

We consider the swelling kinetics of layered structures. We focus on the case of triblock copolymer mesogels, although our results are applicable to other layered structures including clays. We assume the mesogels are swollen by a solvent that is good for the bridging block but poor for the non-bridging block. At long times the penetration front moves as in ordinary diffusion, i.e., as $t^{1/2}$. At short times, however, the bending elasticity of the non-bridging layers becomes important. This bending elasticity leads to a $t^{1/6}$ relaxation of the penetration front at early times. The crossover length between these two regimes is approximately the width of a single layer. However, for a large number of lamellae there is a cooperative effect which leads to a large enhancement of this crossover length.
I. INTRODUCTION

In the strong segregation limit, a symmetric diblock copolymer with A and B blocks will form a lamellar phase consisting of a series of AB layers. This kind of system has received much study and may have applications as a novel composite material. In general, however, it suffers from one major drawback: the AB lamellae are only weakly bonded to one another by local Van der Waals forces, and possibly by a few entanglements. The system thus lacks mechanical integrity in the melt state and the AB interfaces are very weak. This is the case even if both blocks are glassy. If for instance the system is placed in a solvent which is good for the B blocks, these blocks swell and the individual lamellae separate from one another. However, as noted by Halperin and Zhulina [1], one very simple modification allows much greater mechanical integrity. This is to use an ABA triblock copolymer. A certain fraction of the B chains bridge between layers. In the melt state this system, though a liquid, is much more difficult to pull apart, because of the presence of these bridges. If the A regions are rubbery or glassy then the system becomes a solid, even though the B regions may still show liquid-like behavior. When the B regions are swollen by a selective solvent (which is good for B and bad for A), the system becomes a sandwich with rubbery liquid layers between solid regions. This swollen system was given the name “mesogel” [1]. Although the theoretical studies of these systems have been rather recent, mesogels have existed in practice for much longer [2]. Their mechanical integrity offers many advantages over diblock systems, and they are already being used in controlled drug release systems [3].

Previous theoretical studies have concentrated on the equilibrium behaviour and to a lesser extent on the rheology of mesogels [1]. The questions of interest for equilibrium properties are the degree of bridging, the degree of swelling, and the mechanical moduli of the composite system. Here our interest lies in the kinetics of swelling, i.e., the approach to equilibrium. The swelling kinetics of isotropic gels is a subject for which there is a broad literature reporting many novel effects [4-6]. Mesogels, are by definition non-isotropic, and might exhibit interesting swelling behaviour because of this as well as the competition between layer elasticity and solvent penetration. The swelling of lamellar mesogels is related to the swelling of other layered systems such as clays [7]. These have numerous applications, particularly in environmental science. Geometrically the two systems are similar, although there are major differences in both the type and magnitude of the physical forces involved. In clays, for instance, the layers are much smaller and electrostatic and short-range forces are thought to be of great importance. Another related area is the swelling of polymeric glasses. In that case there are two kinds of temporal behaviour, ordinary diffusion and “diffusion” linear in time. There have been many proposals for why this occurs [8,9], all of which agree more-or-less with the experimental results. However, at present there is no widely accepted definitive theory, although elastic effects almost certainly play some role.

In any system involving mesogels the gels must at some time go through a swelling process, and our study is applicable to all such cases. The opposite case where one de-swells a mesogel may be important in drug delivery systems [10]. The same model can be used to describe de-swelling, although we do not discuss it further here. In section II we examine the case of a single layer of a mesogel, such as might be obtained by spin-coating. This turns out to have a mesoscopic length $L_1$, below which the elasticity of the layers needs to be accounted for, and for which the swelling kinetics are non-diffusive in character. It turns out
that \( L_1 \) is of order the layer thickness. In section III we generalise this to more macroscopic multilamellar samples. There, the crossover length becomes much larger: \( L_M \approx M^{1/2}L_1 \), where \( M \) is the number of layers. Hence \( L_M \) can become of macroscopic size. We conclude with a discussion in section IV.

II. THE MODEL OF DIFFUSION PROCESS IN SINGLE LAYER

Consider a melt of ABA triblocks, with blocks of roughly equal length. At low temperatures this system will microphase separate to form a series of distinct B layers separated by A layers, with sharp boundaries in between. In general this will have a large number of defects, which can be removed by shearing. At lower temperatures, or if the A phase is crosslinked, the A region may become a rubbery solid. The system then consists of a series of rubbery A layers separated by molten B layers. This results in a well-ordered “meso-rubber”. This system can be placed in a selective solvent that is good for the B block and poor for the A block. We assume for simplicity that only one edge of the specimen is in contact with the solvent reservoir. The solvent penetrates the B regions and swells them. Here we consider a single ABA lamella. Initial contact of the solvent with the B regions is energetically favourable but is opposed by two effects. The first is the stretching of the B chains to form a brush. The second is the bending and stretching of the surrounding A regions. This implies that the free energy per unit area of the system consists of three terms

\[
F = F_{B\text{\ stretch}} + F_{B\text{\ interaction}} + F_{A\text{\ bend}}. 
\]

Here we ignore the stretching energy of A domains, which is a second-order effect in relaxed layers. We need to evaluate each of these terms in the partially swollen state to describe the swelling kinetics.

Before swelling, the B regions form a dense melt of thickness \( \bar{h} \). After equilibrium swelling is reached, the B regions form a swollen polymer brush [11,12] with the same grafting density as the melt. In the swollen state, dense grafting enforces strong overlap among the undeformed coils. For tethered chains in a good solvent, this increases the number of monomer-monomer contacts and the corresponding interaction energy. This penalty is reduced by stretching the chains along the normal to the grafting sites, thereby lowering the monomer concentration in the layer and increasing the layer thickness \( h \). Stretching lowers the interaction energy per chain, \( F_{B\text{\ interaction}} \), at the price of a higher elastic free energy, \( F_{B\text{\ stretch}} \). The interplay of these two terms sets the equilibrium thickness of the layer \( h_{eq} \).

We write the layer thickness of the B region in the partially swollen state as

\[
h(x) = \bar{h}(1 + \psi(x)), \tag{2}
\]

where \( \psi \) is the solvent concentration in the B region. We can express the volume fraction of solvent \( \phi_s \) and the volume fraction of polymer \( \phi_p \) as \( \phi_s = \psi/(1 + \psi) \) and \( \phi_p = 1/(1 + \psi) \). In the Alexander-de Gennes model, the B layer is envisioned as a close-packed array of blobs of uniform size \( \xi \), which is equal to the grafting distance \( d \). Each of these blobs costs a free energy of \( kT \). The free energy of the B layer per unit area is given by [11]
\[ F_B = F_{B\text{ interaction}} + F_{B\text{ stretch}} \]
\[ = kT\left(\frac{h}{a^3}\right)\phi_p^2 + kT\left(\frac{h^2}{Na^2d^2}\right)\phi_p^{\frac{1}{2}}, \quad (3) \]

where numerical prefactors have been ignored, and \( a \) is the \( B \) monomer size. Since \( \phi_p = (1 + \psi)^{-1} \) and \( h = \bar{h}(1 + \psi) \), Eq. (3) can be rewritten as
\[ F_B = kT\left(\frac{\bar{h}}{a^3}\right)(1 + \psi)^{-\frac{1}{2}} + kT\left(\frac{\bar{h}^2}{Na^2d^2}\right)(1 + \psi)^\frac{1}{2}. \quad (4) \]

Minimising this yields the equilibrium swelling \( \psi_{eq} = \left(\frac{5Nd^2}{7\bar{h}a}\right)^{\frac{1}{4}} - 1 \). It is convenient to simplify \( F_B \) by expanding about \( \psi_{eq} \), to yield an approximate free energy per unit area for the \( B \) regions [13,14]
\[ F_B \approx \frac{1}{2}S(\psi - \psi_{eq})^2. \quad (5) \]

Here, the coefficient \( S \) in Eq. (5) is given by
\[ S = \frac{\partial^2 F_B}{\partial \psi^2} \]
\[ = kT\left(\frac{\bar{h}^2}{Na^2d^2}\right)\left(\frac{\bar{h}a}{Nd^2}\right)^{\frac{1}{2}}. \quad (6) \]

The remaining term in the free energy is the bending elastic energy of the \( A \) regions:
\[ F_A = \frac{1}{2}\kappa \left(\nabla^2 h\right)^2 = \frac{1}{2}\kappa' \left(\nabla^2 \psi\right)^2, \quad (7) \]
where \( \kappa \) is the bending elastic constant and \( \kappa' = \bar{h}^2\kappa \). If the \( A \) regions form a rubbery solid, then we can estimate \( \kappa \) from elasticity theory as \( \kappa \sim \mu_r H_A^3 \) where \( \mu_r \) is the modulus of rigidity of the \( A \) regions and \( H_A \) is the thickness of the \( A \) layers [15]. This modulus is related to the number of crosslinks per unit volume \( n \), by \( \mu_r \sim nkT \).

The chemical potential of the solvent is
\[ \mu = \frac{\delta F}{\delta \psi} \]
\[ = \kappa' \left(\nabla^4 \psi\right) + S(\psi - \psi_{eq}). \quad (8) \]

The solvent current is defined by \( J_s = -\mathcal{M}\nabla \mu \), where \( \mathcal{M} \) is a mobility, which we take to be independent of the concentration \( \psi \) [16]. From the continuity equation
\[ \frac{\partial \psi}{\partial t} + \nabla \cdot J_s = 0, \quad (9) \]
we have the diffusion equation

\[ \frac{\partial \psi}{\partial t} = \nabla \cdot (M \nabla \mu) = \kappa' M (\nabla^6 \psi) + SM (\nabla^2 \psi). \]  

(10)

Here we consider a single layer parallel to the $xy$ plane, with infinite extent in the $y$ direction (Fig. 1). The solvent lies in the region $x < 0$ and the gel in the region $x > 0$. This reduces the problem to one dimension, with spatial gradients only in the $x$ direction.

From Eq. (10), we expect the diffusion process to be dominated by the bending energy at shorter lengthscales (or earlier times), and to be dominated by the interaction energy at longer lengthscales (or later times). Therefore, the diffusion process is characterized by a crossover time scale $T_1$ and a crossover length $L_1$. Depending on the initial conditions, for times less than $T_1$ or for solvent penetration less than $L_1$, the process is not characterized by simple diffusion. Instead, the profile spreads as $t^{1/6}$. At later times, as the solvent profile spreads out, simple diffusion dominates. In most of what follows, we shall be concerned primarily with the non-diffusive regime, and in particular with crossover length, below which it can be observed. We can estimate the crossover length $L_1$ by the substitution $\nabla \rightarrow 1/L_1$.

From Eq. (10), the crossover length is approximately

\[ L_1 \approx \left( \frac{\bar{h}^2 \kappa}{S} \right)^{\frac{1}{4}}. \]  

(11)

In a rubbery solid where $\kappa \simeq kTnH^3_A$, the crossover length $L_1$ becomes

\[ L_1 \approx \left[ nH_A^3 Na^2 d^2 \left( \frac{d}{a} \right)^{\frac{1}{3}} \right]^{\frac{1}{4}}. \]  

(12)

Within the Alexander-de Gennes approximation, the chains are assumed to be equally stretched. The grafting distance is estimated to be

\[ d \simeq \left( \frac{4kT}{\gamma a^2} \right)^{\frac{1}{2}} N^{\frac{2}{3}} a. \]  

(13)

We can also estimate the layer thickness of $A$ domains as

\[ H_A = \frac{Na^3}{d^2} \simeq \left( \frac{4kT}{\gamma a^2} \right)^{\frac{1}{2}} N^{\frac{2}{3}} a. \]  

(14)

The layer thickness of the $B$ domains, prior to swelling is similarly given by $\bar{h} \simeq aN^{2/3}$. Substitution of Eqs. (13) and (14) into Eq. (12) leads to a crossover length.
\[ L_1 \simeq (na^3)^{1/4}N^{13/72}\bar{h} \]  

If we consider a tightly crosslinked network so that \( na^3 \sim 1 \), then the crossover length is roughly the layer thickness \( \bar{h} \). This is a mesoscopic length of order 10^2 to 10^3 Angstroms. Note, however, that if the modulus of the A regions is very large (say, for instance, if the A regions were glassy), then the crossover length \( L_1 \) could be much larger. Before the solvent has reached \( x = L_1 \), we expect the solvent front moves as \( t^{1/6} \). At later times it obeys ordinary diffusion—moving as \( t^{1/2} \). The anomalous \( t^{1/6} \) “diffusion” is a result of the bending elasticity of the A layers. A similar anomalous exponent can be found in the hydrodynamics of membrane systems [17,18].

### III. THE MODEL OF DIFFUSION PROCESS IN MULTILAYERS

In the above we considered the swelling of a single layer. In that case, the A layer elasticity only affected the initial swelling up to a length scale of order of the layer thickness. For a multilayer system, this effect can be much more pronounced. As illustrated in Fig. 2, the swelling of the inner layers is transmitted to the outer layers, and hence the outer layers must bend significantly more. In order to examine this, we first consider the case of uniform swelling, in which each layer is swollen by the same amount at a given value of \( x \). Below, we shall relax this assumption. For \( M \) layers, uniform swelling corresponds to \( \psi_m(x) = \psi(x) \) for \( m = 1, 2, \cdots M \). The height of \( m \)-th layer is given by

\[ h_m(x) = m\bar{h} (1 + \psi(x)). \]  

The free energy of the mesogel is

\[
F = \sum_{m=1}^{M} \left[ \frac{1}{2} \kappa \left( \nabla^2 h_m \right)^2 + \frac{1}{2} S (\psi_m - \psi_{eq})^2 \right],
\]

\[
\simeq \frac{M^3}{6} \kappa' \left( \nabla^2 \psi \right)^2 + \frac{SM^2}{2} (\psi - \psi_{eq})^2. \]

Thus

\[
\frac{\partial \psi}{\partial t} \simeq \kappa' M^3 \frac{3}{3} \nabla^6 \psi + SM \nabla^2 \psi. \]

In other words, the relaxation rate for a mode of wavevector \( q \) in the \( x \) direction, is

\[
\tau_q^{-1} \simeq M \left( \kappa' \frac{M^3}{3} q^6 + SMq^2 \right). \]

The characteristic length \( L_M \), beyond which the swelling becomes dominated by ordinary diffusion, is found by equating the two terms on the right hand side of (19) with \( q = 1/L_M \), and is
Where $L_1$ is the crossover length for a single layer. For a large number, $M$, of layers, this is a lengthscale much larger than the thickness of a single lamella. However, since we consider the case of swelling that occurs from an edge, our results are valid for a mesoscopic crossover length $L_M$ less than the horizontal dimensions of the sample in Fig. 2. The corresponding crossover time is

$$
\tau_M \sim M\bar{h}^2/D,
$$

where $D$ is the diffusion constant for the solvent.

To go beyond the approximation of uniform swelling, we express the height of the $m$-th layer in a more general form

$$
h_m(x) - h_{m-1}(x) = \bar{h}(1 - \psi_m(x)),
$$

where $m = 1, 2, \cdots M$, and $h_0 \equiv 0$. The free energy of the mesogel is

$$
F = \frac{1}{2} \sum_{m=1}^M \left\{ \kappa \left( \nabla^2 h_m \right)^2 + \frac{S}{\bar{h}^2} \left[ h_m - h_{m-1} - \bar{h}(1 + \psi_{eq}) \right]^2 \right\}.
$$

The chemical potential of $l$-th layer can be calculated as

$$
\mu_l = \sum_{m=1}^M \frac{\delta F}{\delta h_m(x)} \frac{\partial h_m(x)}{\partial \psi_l(x)}
= \kappa \bar{h} \sum_{m=l}^M \nabla^4 h_m + \frac{S}{\bar{h}} \sum_{m=l}^{M-1} (2h_m - h_{m+1} - h_{m-1}) + \frac{S}{\bar{h}} \left[ h_M - h_{M-1} - \bar{h}(1 + \psi_{eq}) \right].
$$

The dynamical equations for $h_l$ are given by

$$
\frac{\partial (h_l - h_{l-1})}{\partial t} = \mathcal{M} \bar{h}^2 \kappa \sum_{m=l}^M \nabla^6 h_m + \mathcal{M} S \sum_{m=l}^{M-1} \nabla^2 (2h_m - h_{m+1} - h_{m-1}) + \mathcal{M} S \nabla^2 (h_M - h_{M-1}),
$$

and

$$
\frac{\partial (h_M - h_{M-1})}{\partial t} = \kappa \mathcal{M} \bar{h}^2 \nabla^6 h_M + \mathcal{M} S \nabla^2 (h_M - h_{M-1}).
$$

For large $M$ and small displacements of the layer heights away from their initial positions, we characterize the layer heights by a displacement field $u(x, z)$:

$$
h_m(x) = m\bar{h} + u(x, m\bar{h}),
$$

Eq. (25) becomes
\[
\frac{\partial}{\partial t} \left( \frac{\partial^2 u}{\partial z^2} \right) = -\mathcal{M} \kappa \nabla^6 u(x, z) + \mathcal{M} S \nabla^2 \left( \frac{\partial^2 u}{\partial z^2} \right)
\] (28)

after differentiating once with respect to \(z\). (A discrete expression of this can also be obtained by subtraction of Eq. (25) for adjacent \(l\).) If we express the displacement field \(u(x, z)\) as a sum over wavevectors in the \(x\) and \(z\) directions, \(q\) and \(k_z\),

\[
u (x, z) = \sum_{q, k_z} \tilde{u}(q, k_z) e^{i(qx+k_z z)},
\] (29)

then the relaxation rate as a function of \(q\) and \(k_z\) is

\[
\tau_q^{-1} = \mathcal{M} \kappa q^6 k_z^{-2} + \mathcal{M} S q^2.
\] (30)

The initial swelling mode corresponds to the smallest value of \(k_z\) consistent with the boundary conditions, namely

\[
k_z \approx \frac{1}{M \bar{h}}.
\] (31)

Thus, the crossover length is

\[
L_M \approx \left( \frac{\kappa \bar{h}^2}{S M^2} \right)^{\frac{1}{4}} \approx M^{\frac{3}{2}} L_1.
\] (32)

i.e. the same result as was found in the uniform swelling case (20).

Equation (23) can also be expressed in terms of the concentration variables \(\psi_m(x)\):

\[
F = \frac{1}{2} \sum_{m=1}^{M} \left\{ \kappa \left( \nabla^2 h_m \right)^2 + S \left( \psi_m - \psi_{eq} \right)^2 \right\},
\] (33)

where

\[
h_m = \bar{h} \sum_{l=1}^{m} \left( 1 + \psi_l (x) \right).
\] (34)

The chemical potential of \(l\)-th layer is given by

\[
\mu_l = \kappa \bar{h}^2 \sum_{m=l}^{M} \sum_{m'=l}^{m} \nabla^4 \psi_{m'} + S \left( \psi_l - \psi_{eq} \right).
\] (35)

The dynamical equations for \(\psi_l\) can be expressed as

\[
\begin{pmatrix}
\frac{\partial}{\partial t} \psi_1 \\
\vdots \\
\frac{\partial}{\partial t} \psi_{M-1} \\
\frac{\partial}{\partial t} \psi_M
\end{pmatrix} = \kappa \bar{h}^2 \mathcal{M} 
\begin{pmatrix}
M & \cdots & 2 & 1 \\
\vdots & \vdots & \vdots & \vdots \\
2 & \cdots & 2 & 1 \\
1 & \cdots & 1 & 1
\end{pmatrix}
\begin{pmatrix}
\nabla^6 \psi_1 \\
\vdots \\
\nabla^6 \psi_{M-1} \\
\nabla^6 \psi_M
\end{pmatrix} + \mathcal{M} 
\begin{pmatrix}
\nabla^2 \psi_1 \\
\vdots \\
\nabla^2 \psi_{M-1} \\
\nabla^2 \psi_M
\end{pmatrix}.
\] (36)
At early times, for which the spatial gradients are large, the dominant relaxation rate corresponding to a mode of wavevector \( q \) is

\[
\tau_q^{-1} = \kappa \bar{h}^2 \mathcal{M} \lambda^{(\text{max})} q^6 + S \mathcal{M} q^2,
\]

(37)

where \( \lambda^{(\text{max})} \) is the largest eigenvalue of the matrix

\[
\begin{pmatrix}
M & \cdots & 2 & 1 \\
\vdots & & \vdots & \vdots \\
2 & \cdots & 2 & 1 \\
1 & \cdots & 1 & 1
\end{pmatrix}.
\]

(38)

It can be shown that the eigenvalues of this matrix are given by [19]

\[
\lambda = \frac{1}{2} \left( 1 - \cos \omega \right),
\]

(39)

where \( \omega \) satisfies

\[
\tan (M \omega) = \cot \frac{\omega}{2}.
\]

(40)

Thus, for large \( M \), the leading eigenvalue is

\[
\lambda^{(\text{max})} \approx \frac{4}{\pi^2} M^2 \left( 1 + \frac{1}{M} \right).
\]

(41)

(This was also determined by numerical evaluation of \( \lambda^{(\text{max})} \) for \( M \) up to 100.) Thus, the crossover length

\[
L_M \approx L_1 M^{1/2} \left( 1 + \frac{1}{4M} \right).
\]

(42)

On simple physical grounds it is expected that the anomalous swelling at early times will be most apparent for the inner layers, since the curvature elasticity of the outer layers tends to constrain the inner layers. In other words, the initial relaxation of a profile such as the one shown in Fig. 2 will be dominated by a mode that relaxes gradients of the inner layers \((h_1(x), h_2(x), \ldots)\) faster than the outer layers \((\ldots, h_{M-1}(x), h_M(x))\). This is reflected in the eigenvector corresponding to this mode (Eq. [41]), which is given by

\[
\psi_l^{(\text{max})} \propto \sin \left( \frac{(M - l + 1)\pi}{2M} \right).
\]

(43)

Thus, indeed the initial relaxation of the inner layers (small \( l \)) is greater than that of the outer layers (large \( l \)). However, the crossover length in Eq. (42) still grows as \( M^{1/2} \), as for uniform swelling.
IV. DISCUSSION

In this paper we have examined the swelling kinetics of lamellar mesogels. For such mesogels the elasticity of the solid lamellae leads to a novel kinetics which is non-diffusive at short times. Similar effects should be important for the swelling of clays and other layered structures. There is one better-known case of non-diffusive behaviour, and that occurs in the swelling of isotropic polymer glasses [8,9]. In that system there occurs both case I behaviour, which obeys ordinary diffusion, and case II behaviour where the front moves linearly in time. There is even a “super-case II” behaviour which has a front position moving as $t^{3/2}$. In general the explanations of case II involve either a diffusion constant which strongly depends on concentration, or a stress relation which similarly depends strongly on the concentration. Lamellar mesogels represent a totally different type of behaviour, where the front moves as $t^{1/6}$, at early times and as $t^{1/2}$ at later times. Note that here we have ignored the dependence of the diffusion constant on concentration and have expanded the free energy about the equilibrium state. Our results are thus most applicable to the situation where the meso-rubber is first pre-swollen and then swollen again to reach an equilibrium swelling. However, the general effect of the $A$ layer elasticity will always be to modify the swelling at early times. We have also ignored cracks in our analysis. If the strains set up in the system are very large then cracks may appear in the $A$ region. Such cracks are indeed seen in the swelling of polymer glasses, which can swell explosively.

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We note that a cubic term may play an important role for the compression of non-bridging brushes, as suggested by the self-consistent field theory [14]. For triblock copolymer mesogels, however, the B regions consist of bridging and non-bridging B chains. Those B chains bridging different A domains should have a step-function profile. Therefore, for small deviations from equilibrium, we expect that the leading term in the free energy is the quadratic term.

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FIGURES

FIG. 1. The swelling geometry for a single layer. The solvent penetrates from the left and the gel is assumed infinite towards the right and out of the plane of the page. The swelling profile is characterized by \( h(x) \).

FIG. 2. The swelling geometry for multiple layers. Note that in this case the swelling of the inner layers causes a large bending at the outer layers.