SUPPORTING INFORMATION. Line Roughness in Lamellae-Forming Block Copolymer Films

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I. The correlation coefficient in reciprocal space, C_k.

In the text, we pointed that the expressions in eq. 3 and eq. 5 in the main text form a parallel set in real and reciprocal space:

Real Space	Reciprocal Space
$\sigma_w^2 = 2\sigma_\varepsilon^2 - 2c\sigma_\varepsilon^2$ (S1)	$G_w(f_k) = 2G_\varepsilon(f_k) - 2C_k G_\varepsilon(f_k)$ (S4)
$\sigma_p^2 = \frac{1}{2}\sigma_\varepsilon^2 + \frac{1}{2}c\sigma_\varepsilon^2$ (S2)	$G_p(f_k) = \frac{1}{2}G_\varepsilon(f_k) + \frac{1}{2}C_k G_\varepsilon(f_k)$ (S5)
$\sigma_\varepsilon^2 = \frac{\sigma_w^2}{4} + \sigma_p^2$ (S3)	$G_\varepsilon(f_k) = \frac{G_w(f_k)}{4} + G_p(f_k)$ (S6)

Where c is related to the covariance of the two edges in a line:

$$c = \frac{\mathrm{cov}(\varepsilon 1, \varepsilon 2)}{\sigma_{\varepsilon 1} \cdot \sigma_{\varepsilon 2}} \qquad \text{(S7)}$$

And the covariance is given by:

$$\mathrm{cov}(\varepsilon 1, \varepsilon 2) = \frac{1}{N} \sum_j (\varepsilon 2_j - \overline{\varepsilon 2})(\varepsilon 1_j - \overline{\varepsilon 1}) \qquad \text{(S8)}$$

And C_k is a corresponding correlation coefficient in reciprocal space. In this section, we will demonstrate that the parallel relations hold true at every frequency and we will also demonstrate that C_k is the Cosine of the phase difference between the Fourier components of the opposite edges at frequency f_k.

Eq S1 and eq S2 are straightforward to derive[1] substituting the width and placement definitions (eq 1 in the main text) into the definition of variance (eq 2 in the main text). We illustrate here the example of eq S1. According to eq 1 and 2 in the main text:

$$\begin{aligned}
\sigma_w^2 &= \frac{1}{N} \sum_j \left(w_j - \overline{w}\right)^2 \\
\sigma_w^2 &= \frac{1}{N} \sum_j \left(\varepsilon 2_j - \varepsilon 1_j - (\overline{\varepsilon 2} - \overline{\varepsilon 1})\right)^2 \\
\sigma_w^2 &= \frac{1}{N} \sum_j \left((\varepsilon 2_j - \overline{\varepsilon 2}) - (\varepsilon 1_j - \overline{\varepsilon 1})\right)^2 \\
\sigma_w^2 &= \frac{1}{N} \sum_j \left((\varepsilon 2_j - \overline{\varepsilon 2})^2 + (\varepsilon 1_j - \overline{\varepsilon 1})^2 - 2(\varepsilon 2_j - \overline{\varepsilon 2})(\varepsilon 1_j - \overline{\varepsilon 1})\right) \\
\sigma_w^2 &= \sigma_{\varepsilon 1}^2 + \sigma_{\varepsilon 2}^2 - 2\frac{1}{N} \sum_j (\varepsilon 2_j - \overline{\varepsilon 2})(\varepsilon 1_j - \overline{\varepsilon 1}) \\
\sigma_w^2 &= \sigma_{\varepsilon 1}^2 + \sigma_{\varepsilon 2}^2 - 2\,\mathrm{cov}(\varepsilon 1, \varepsilon 2)
\end{aligned} \qquad \text{(S9)}$$

Where in the last line of eq S9 we substituted eq S8 in the last term. Then we substitute the linear correlation coefficient from eq S7 into the last line of eq S9 to obtain:

$$\sigma_w^2 = \sigma_{\varepsilon 1}^2 + \sigma_{\varepsilon 2}^2 - 2\,\mathrm{cov}(\varepsilon 1, \varepsilon 2) \cdot \frac{\sigma_{\varepsilon 1}\sigma_{\varepsilon 2}}{\sigma_{\varepsilon 1}\sigma_{\varepsilon 2}} \qquad \text{(S10)}$$

$$\sigma_w^2 = \sigma_{\varepsilon 1}^2 + \sigma_{\varepsilon 2}^2 - 2c\sigma_{\varepsilon 1}\sigma_{\varepsilon 2}$$

Recalling that for self-similar lines in the limit of large *N*: $\sigma_{\varepsilon 1}^2 = \sigma_{\varepsilon 2}^2 = \sigma_\varepsilon^2$, then we obtain the familiar form of eq S1:

$$\sigma_w^2 = 2\sigma_\varepsilon^2 - 2c\sigma_\varepsilon^2 \qquad \text{(S11)}$$

Now, to obtain eq S3, we first rewrite eq S1:

$$c = \frac{2\sigma_\varepsilon^2 - \sigma_w^2}{2\sigma_\varepsilon^2} \qquad \text{(S12)}$$

Now we rewrite eq S2:

$$c = \frac{2\sigma_p^2 - \sigma_e^2}{\sigma_\varepsilon^2} \qquad \text{(S13)}$$

Equating eq S12 to S13 and solving for σ_ε^2:

$$\sigma_\varepsilon^2 = \frac{\sigma_w^2}{4} + \sigma_p^2 \qquad \text{(S14)}$$

Which is the same as eq S3.

Now we proceed to do a similar exercise in reciprocal space. First we start with the power spectral density (PSD) of the width roughness, G_w. From the definition of the PSD explained in eq 4 of the main text:

$G_w(f_k) = \frac{2\Delta}{N^2}|W_k|^2; \quad k = 1, 2 \ldots \frac{N}{2} - 1$ (S15)

Where W_k are the Fourier coefficients given by:

$$W_k = \sum_j w_j e^{i2\pi \cdot jk/N} \qquad \text{(S16)}$$

Recall from the definition of eq 1 in the main text: $w_j = \varepsilon 2_j - \varepsilon 1_j$,

$$\begin{aligned} W_k &= \sum_j (\varepsilon 2_j - \varepsilon 1_j) e^{i2\pi \cdot jk/N} \\ W_k &= \sum_j \varepsilon 2_j e^{i2\pi \cdot jk/N} - \sum_j \varepsilon 1_j e^{i2\pi \cdot jk/N} \end{aligned} \qquad \text{(S17)}$$

Note that each term in eq S17 corresponds to the Fourier coefficients of each line edge, thus:

$$W_k = E2_k - E1_k \qquad \text{(S18)}$$

Note the parallel form of eq (S18) with the definition of eq 1 in the main text: $w_j = \varepsilon 2_j - \varepsilon 1_j$.

Next we substitute eq S18 into eq S15 (in what follows, to simplify the notation, we restrict the expressions to the range $k = 1, 2 \ldots \frac{N}{2} - 1$. We will leave the special cases of k = 0 and k =N/2 as an exercise to the interested reader):

$$G_w(f_k) = \frac{2\Delta}{N^2}\left| E2_k - E1_k \right|^2 \qquad \text{(S19)}$$

$$G_w(f_k) = \frac{2\Delta}{N^2}(|\mathrm{E1}_k|^2 + |\mathrm{E2}_k|^2 - \mathrm{E1}_k E2_k^* - E1_k^* \mathrm{E2}_k) \qquad \text{(S20)}$$

Note that the first two terms in eq S20 are the PSD of each line edge: $G_\varepsilon(f_k) = \frac{2\Delta}{N^2}|E_k|^2$, therefore, eq S20 can be written as:

$$G_w(f_k) = G_{\varepsilon1}(f_k) + G_{\varepsilon2}(f_k) - \frac{2\Delta}{N^2}(\mathrm{E1}_k E2_k^* + E1_k^* \mathrm{E2}_k) \qquad \text{(S21)}$$

Note the parallel relationship of eq S21 with the last line of eq S9. If we take the last term in eq S21 to be the parallel representation of the covariance, it is therefore natural to propose the parallel correlation coefficient in reciprocal space:

$$C_k = \frac{\mathrm{E1}_k \mathrm{E2}_k^* + \mathrm{E1}_k^* \mathrm{E2}_k}{|\mathrm{E1}_k|^2 + |\mathrm{E2}_k|^2} \qquad \text{(S22)}$$

Substituting eq S22 into eq S21,

$$G_w(f_k) = G_{\varepsilon1}(f_k) + G_{\varepsilon2}(f_k) - C_k \frac{2\Delta}{N^2}(|\mathrm{E1}_k|^2 + |\mathrm{E2}_k|^2) \qquad \text{(S23)}$$

Recalling that for self-similar lines in the limit of large *N*, $|\mathrm{E1}_k| = |\mathrm{E2}_k| = |\mathrm{E}_k|$ and $G_{\varepsilon1}(f_k) = G_{\varepsilon2}(f_k) = G_\varepsilon(f_k)$, then eq S23 becomes

$$G_w(f_k) = 2G_\varepsilon(f_k) - 2C_k \frac{2\Delta}{N^2}|\mathrm{E}_k|^2 \qquad \text{(S24)}$$

And using the definition of the PSD: $G_\varepsilon(f_k) = \frac{2\Delta}{N^2}|E_k|^2$ and substituting into eq S24:

$$G_w(f_k) = 2G_\varepsilon(f_k) - 2C_k G_\varepsilon(f_k) \qquad \text{(S25)}$$

Which demonstrates eq S4.

We leave it as an exercise for the interested reader to show the corresponding relationships for the PSD of the line placement G_p: First, it can be shown that in analogy to eq 1 in the main text:

$$P_k = \frac{1}{2}E1_k + \frac{1}{2}E2_k \qquad \text{(S26)}$$

Then one can prove eq S5. Next, combining eq S4 and S5 one obtains eq S6.

Experimentally, once G_w and G_p are computed, one can obtain C_k without keeping track of the complex Fourier coefficients $\mathrm{E1}_k^*$ or $\mathrm{E2}_k^*$. By solving for G_ε in eq S4 and substituting into eq S5, one arrives at the convenient expression for C_k:

$$C_k = \frac{4G_p(f_k) - G_w(f_k)}{4G_p(f_k) + G_w(f_k)} \qquad \text{(S27)}$$

Which is what we used in the main text eq 6 (naturally, there is a parallel expression in real space: $c = \frac{4\sigma_p^2 - \sigma_w^2}{4\sigma_p^2 + \sigma_w^2}$).

Now, to understand the meaning of C_k, we proceed to simplify eq S22. Since every Fourier coefficient is a complex number, let's define:

$$\begin{aligned} \mathrm{E1_k} &= |\mathrm{E1_k}| e^{i\alpha 1_k} \\ \mathrm{E2_k} &= |\mathrm{E2_k}| e^{i\alpha 2_k} \end{aligned} \qquad \text{(S28)}$$

Where $\alpha 1_k$ and $\alpha 2_k$ are the phase values of the Fourier components of the first and second line edges at frequency k. Then we substitute eq S28 into eq S22:

$$C_k = \frac{|\mathrm{E1}_k||\mathrm{E2}_k|(e^{i(\alpha 1_k - \alpha 2_k)} + e^{-i(\alpha 1_k - \alpha 2_k)})}{|\mathrm{E1}_k|^2 + |\mathrm{E2}_k|^2} \qquad \text{(S29)}$$

Recalling again that for self-similar lines in the limit of large N: $|\mathrm{E1}_k| = |\mathrm{E2}_k| = |\mathrm{E}_k|$ and thus eq S29 can be simplified as:

$$C_k = \frac{|\mathrm{E}_k|^2 \; 2\mathrm{Cos}(\alpha 1_k - \alpha 2_k)}{2|\mathrm{E}_k|^2} \qquad \text{(S30)}$$

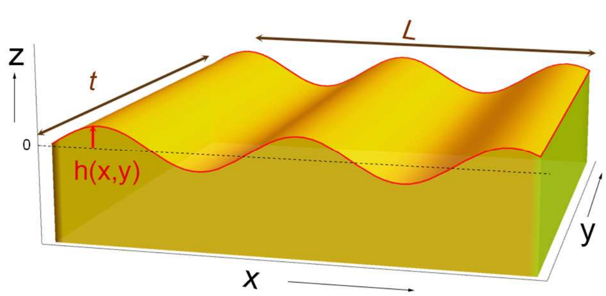
$C_k = \mathrm{Cos}(\alpha 1_k - \alpha 2_k)$ (S31)

Therefore, C_k represents the Cosine of the phase difference between the Fourier components of opposite edges at frequency k. In the same way as its real space analog (c), C_k ranges from 1 to -1. When the two Fourier components of opposite edges are perfectly in phase ($\alpha 1_k = \alpha 2_k$), they are fully correlated and $C_k=1$. When $|\alpha 1_k - \alpha 2_k| = \pi$, they are fully anti-correlated and $C_k=-1$.

It is interesting to note that while the phase information of each E_k is lost in the PSDs, the phase difference is still preserved in C_k and can be recovered from the PSDs through eq S27.

II Thermal fluctuation in a 1D membrane.

In this section we derive the thermal fluctuation modes for a 1D interface to show that the expression differs from the 2D version only by a constant given by $1/t$, where t is the film thickness. We follow the treatment shown by Safran[2]. To simplify notation, we calculate here the thermal fluctuations of an interface (interfacial or capillary modes only). Extension to the membrane is straight forward by adding the curvature term for undulations and curvature and volume terms for peristaltic modes.[3]



Consider the surface of Figure S1. The equilibrium flat surface is set to be parallel to the x-y plane. The height of the interface is represented as z = *h(x,y)*. or z = $h(\vec{r})$ where $\vec{r}$ is the position vector. The dimension of the surface is *L* along the x-axis and *t* along the y-axis (in our experiments, t is the thickness of the film). We represent the partial derivatives of *h* as:

$$h_x = \frac{\partial h}{\partial x}; \quad h_y = \frac{\partial h}{\partial y} \quad \text{(S32)}$$

In the Monge gauge, the Area of the surface is:

$$A = \iint dx \cdot dy\sqrt{1 + h_x^2 + h_y^2} \approx \iint dx \cdot dy(1 + \frac{1}{2}h_x^2 + \frac{1}{2}h_y^2) \qquad \text{(S33)}$$

Given an interfacial energy, γ, the free energy of the interface is given by:

$$F_s = \gamma A \approx \gamma \iint dx \cdot dy(1 + \frac{1}{2}h_x^2 + \frac{1}{2}h_y^2) \qquad \text{(S34)}$$

Which can be separated in two terms:

$$F_s \approx \gamma \iint dx \cdot dy + \gamma \iint dx \cdot dy\left(\frac{1}{2}h_x^2 + \frac{1}{2}h_y^2\right) = F_0 + \Delta F_s \quad \text{(S35)}$$

Where the first term is a constant given by the size of the interface on the x-y plane ($F_o = \gamma L t$). The second term is the excess free energy ΔF_s arising from the surface roughness. Thus,

$$\Delta F_s = \gamma \iint dx\, dy\left(\frac{1}{2}h_x^2 + \frac{1}{2}h_y^2\right) \qquad \text{(S36)}$$

Now we proceed to calculate the thermal fluctuations of the interface for the one-dimensional case. Note that by "one-dimensional" we mean that the interface has no fluctuations along the y-direction: $h_y = \frac{\partial h}{\partial y} = 0$, just like in the schematic of Fig. S1 This interpretation of 1D is needed because γ is still a surface term. We now follow the treatment shown in chapter 3.3 of the textbook by Safran[2] but with the condition that $h(\vec{r}) = h(x)$ and $h_y = 0$.

Let's start by rewriting the excess free energy of eq S36 for the 1D case:

$$\Delta F_s = \gamma \int dy \int dx \frac{1}{2} h_x^2$$
$$\Delta F_s = \frac{1}{2} \gamma t \int dx h_x^2 \qquad \text{(S37)}$$

We also use the same Fourier pairs as Safran, but noting that they are now 1D:

$$h(x) = \frac{1}{\sqrt{L}} \sum_q h(q) e^{iq \cdot x}$$
$$h(q) = \frac{1}{\sqrt{L}} \int dx\, h(x) e^{-iq \cdot x} \qquad \text{(S38)}$$

Where L is the length of the interface along the x-axis and q is the 1D wave vector. Note that $h(x)$ has units of [length] while $h(\vec{q})$ has units of $[\text{length}]^{3/2}$. Now our goal is to express eq S37 in reciprocal space. First, we calculate h_x using eq S38:

$$h_x = \frac{1}{\sqrt{L}} \sum_q h(q) \frac{\partial}{\partial x} \left(e^{iq \cdot x} \right)$$
$$h_x = \frac{1}{\sqrt{L}} \sum_q h(q)\, iq\, e^{iq \cdot x} \qquad \text{(S39)}$$

Now we calculate $(h_x)^2$:

$$h_x^2 = \left(\frac{1}{\sqrt{L}} \right)^2 \left(\sum_q h(q)\, iq\, e^{iq \cdot x} \right) \left(\sum_{q'} h(q')\, iq'\, e^{iq' \cdot x} \right)$$
$$h_x^2 = \frac{-1}{L} \sum_q \sum_{q'} h(q) h(q')\, q\, q'\, e^{ix(q+q')} \qquad \text{(S40)}$$

Now substituting back into eq S37:

$$\Delta F_s = \frac{-1}{2L} \gamma t \int dx \left(\sum_q \sum_{q'} h(q) h(q')\, q\, q'\, e^{ix(q+q')} \right)$$
$$\Delta F_s = \frac{-1}{2L} \gamma t \left(\sum_q \sum_{q'} h(q) h(q')\, q\, q' \right) \int dx\, e^{ix(q+q')} \qquad \text{(S41)}$$

Note that $\int dx\, e^{ix(q+q')} = L\, \delta(q + q')$, so the integral is equal to L when $q' = -q$ and it is zero otherwise. Thus, we can rewrite eq S41:

$$\Delta F_s = \frac{1}{2} \gamma t \sum_q h(q)\, q^2\, h(-q) \qquad \text{(S42)}$$

Following the thermodynamic arguments explained by Safran[2], if the Hamiltonian (the energy of the system) is of the form:

$$H = \frac{1}{2} \sum_q h(\vec{q})\, g(\vec{q})\, h(-\vec{q}) \qquad \text{(S43)}$$

Then by virtue of the equipartition theorem, the power spectrum of the fluctuations is given by:

$$\langle |h(\vec{q})|^2 \rangle = \frac{k_B T}{g(\vec{q})} \qquad \text{(S44)}$$

Where k_B is the Boltzmann constant. The corresponding average in real space is given by:

$$\langle h(\vec{r})^2 \rangle = \frac{1}{L^d} \sum_q \langle |h(\vec{q})|^2 \rangle \qquad \text{(S45)}$$

Where, according to Safran, d is the dimensionality of the system. We point out that eq S44 is the power spectral density of the fluctuations as presented in the main text. Similarly, eq S45 corresponds to the variance.

Going back to our particular example, by comparing eq S42 to eq S43, we see that for our problem, the function $g(q)$ is given by:

$$g(q) = \gamma t q^2 \qquad \text{(S46)}$$

Therefore the PSD of the fluctuations from eq S44 is given by:

$$\langle |h(\vec{q})|^2 \rangle = \frac{k_B T}{\gamma t q^2}$$
$$\langle |h(\vec{q})|^2 \rangle = \frac{k_B T/t}{\gamma q^2} \qquad \text{(S47)}$$

Comparing eq S47 with the 2D result by Safran[2], we see that the only difference is the factor *1/t* that was a consequence of the fact that $h_y = 0$. Other than that, the functional form is the same with the same available modes.

The exercise done here can be extended to include the energy from the curvature of a membrane (see Safran) to obtain the expression for the undulatory modes $G_{und}(f_k)$ as shown in the main text (eq 10 main text), but the reader can quickly identify the 1/t term that has the same origin as in this simpler example.

Finally note that the PSD units in the 1D case (eq S47) are $[\text{length}]^3$ while in the corresponding 2D case (see Safran) they would be $[\text{length}]^4$.

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