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Abstract. This paper was written to postgraduate students of Physics. It is shown didactically how to calculate rigorously the wrinkling wavelengths observed when rigid thin films are deposited on soft elastic substrates. Our predictions are compared with DLC films deposited on PDMS substrates.
Key words: *wrinkling wavelengths; thin films.*

(I) Introduction.

In basic courses of Physics and Engineering we learned that it is not enough only know the **forces** applied on a structure.[1] It is also necessary to know the **tensions** and the **deformations** that they produce. All real substances are deformed under the influence of a forces and tensions. The part of Physics that studies these changes is usually known as "Theory of Elasticity."[2,3] As this theme has been extensively studied in many books and papers we will make a brief review only of basic concepts adopted in the theory of elasticity. The mechanics of solid bodies, regarded as continuous media, forms the content of the Theory of Elasticity. [1,2,3]

So, let us consider a bar of length ℓ_o with cross section area A submitted to a force F applied perpendicularly over the area A. We define **stress** $\sigma = F/A$ (force / area). If, under the action of force, the bar undergoes a longitudinal strain ε_ℓ (**strain**) (compression or distension) given by $\varepsilon_\ell = |\Delta\ell| / \ell_o = |\ell - \ell_o|/\ell_o$ we define **modulus of elasticity** or **Young modulus** by

$$E = \sigma/(\Delta\ell/\ell_o) = \sigma/\varepsilon_\ell \qquad (I.1).$$

If the bar undergoes a longitudinal **strain** $\boldsymbol{\varepsilon_\ell} = \Delta\ell/\ell o$ and a transverse strain $\varepsilon_t = \Delta e/e_o$ the relationship between the two deformations is defined as **"Poisson's coefficient"** (ν):[4]

$$\nu = - (\Delta e/e_o) / (\Delta\ell/\ell_o) = - \varepsilon_t /\varepsilon_\ell \qquad (I.2).$$

If a body is deformed from an angle φ due to a **shear stress** σ we define **shear strain** by $\varepsilon_\varphi = \Delta x/\ell_o$. The **shear modulus** of the material due to the **strain** ε_φ is defined by G = μ:

$$G = \mu = \sigma/(\Delta x/\ell_o) = \sigma/\varepsilon_\varphi \qquad (I.3).$$

The **shear modulus** is also known as **Stiffness modulus** or **torsion modulus.**

A body with volume V_o submitted to a hydrostatic pressure P suffers a **volumetric strain** $\varepsilon_V = \Delta V/V_o = (V-V_o)/V_o$. The **volumetric modulus** K or **bulk modulus** (B) is defined by

$$K = B = - P/(\Delta V/Vo) = - P/\varepsilon_V \qquad (I.4).$$

The inverse of the **bulk modulus (**K = B**)** is called **compressibility** k :

$$k = 1/B = 1/K \qquad (I.5).$$

One can show[4] the following **Lamé relations** between B, G, E and ν:

$$K = B = E/3(1-2\nu) \qquad (I.6).$$

and

$$\mu = G = E/2(1+\nu) \qquad (I.7).$$

In reference [4] are seen **Lamé relations** between all elasticity coefficients.

(1) Element of Volume Submitted to an External Force F.

Under the action of applied forces, the solid bodies exhibit deformation to some extent, i.e. they change in shape and volume. The deformation of a body is described mathematically as follows. The position of any point P in the body is defined by its position vector **r** ≡ (x_1, x_2, x_3) in some coordinate system. When the body is deformed, every point is in general displayed. The position of P after the deformation will be **r´**(with coordinates x'_i). The displacement of this point P due to the deformation is given by the vector **u = r´- r,** called **displacement vector** which is a given function of x_i, that is, **u** = **u**(x_i). This means that the coordinates x'_i of the displaced point P are functions of the coordinates x_i.[3]

When a body is deformed the distances between its points change. Let us consider two points very close together. If before the deformation we have distances dx_i these distances after the deformation would be given by $dx'_i = dx_i + du_i$. The original distance between the points $d\ell = \sqrt{dx_i^2}$ after the deformation would be given by $d\ell' = \sqrt{dx'^2_i}$. Since $dx'_i = dx_i + du_i$ and that $du_i = (\partial u_i/\partial x_k)dx_k$ we get

$$d\ell'^2 = d\ell^2 + 2u_{ik}\, dx_i\, dx_k \qquad (1.1),$$

where u_{ik} is a symmetric tensor named **strain tensor** given by

$$u_{ik} = (1/2)[\,(\partial u_i/\partial x_k) + (\partial u_k/\partial x_i) + (\partial u_\ell/\partial x_i)(\partial u_\ell/\partial x_k)] \qquad (1.2).$$

Let us consider a cubic element of volume $\Delta V = \Delta x\, \Delta y\, \Delta z$ of a body. When submitted to an external force it creates **stresses** σ_{ij} along the cube surfaces seen in **Figure 1** generating **tensor strains** u_{ik} given by (1.2).

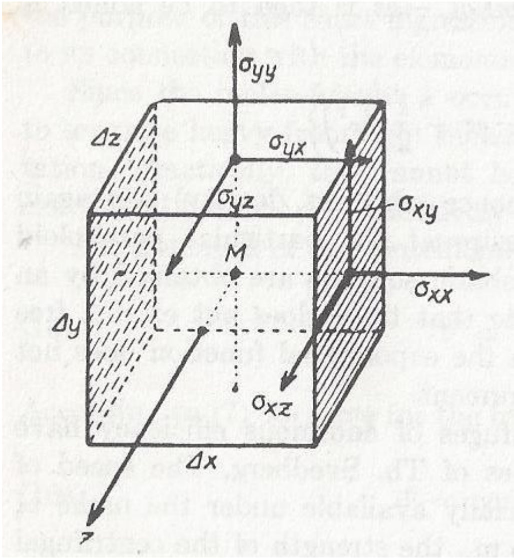

Figure 1. The strain tensor on the cube surfaces. The resulting moment of the shear forces must vanish.[2]

When $\mathbf{u} = \mathbf{u}(x,y,z)$ are very small deformations products like $(\partial u_i/\partial x_k)(\partial u_k/\partial x_i)$ can be neglected and (1.2) can be written as

$$u_{ik} = (1/2)\ \{\partial u_i/\partial x_k) + (\partial u_k/\partial x_i)\} \qquad (1.3).$$

Any deformation can be represented as the sum of a pure shear and a hydrostatic compression. To do so we need only to use the identity[3]

$$u_{ik} = [u_{ik} - (1/3)\delta_{ik}\, u_{\ell\ell}\,] + (1/3)\,\delta_{ik}\, u_{\ell\ell} \qquad (1.4).$$

The first term on the right is evidently a **pure shear**, since the sum of its diagonal terms is zero ($\delta_{ii} = 0$). The second is a **hydrostatic compression**.

(2) Force Ƒ on the Body.

Thus, for any portion of the body, each of the three force components ∫$Ƒ_i$ dV of the resultant of all the internal stresses can be transformed into an integral over the surface. As is known from vector analysis, the integral of a scalar over an arbitrary volume can be transformed into an integral over the surface if the scalar is a divergent of a vector. In our present case we have integral of a vector, and not of a scalar. Hence, the vector $Ƒ_i$ must be the divergent of a tensor of rank 2, that is[3,5]

$$Ƒ_i = \partial\sigma_{ik}/\partial x_k \qquad (2.1).$$

So, the force on any volume of the body can be written as an integral over a closed surface bounding that volume: [3]

$$\int_V Ƒ_i \, dV = \int_V (\partial\sigma_{ik}/\partial x_k)dV = \int_S \sigma_{ik} \, da_k \qquad (2.2),$$

where $\sigma_{ik}\, da_k$ is the i^{th} component of the force on the surface element d**a**.

(3) Free Energy of the Thermodynamic Deformation.

Assuming valid Hooke´s law, a general expression according to Thermodynamics of the free energy F **per unit of volume** of a deformed **isotropic body** is obtained summing two independent squared scalars of two components:[3] one due to **pure shear** and another due to pure **hydrostatic compression** shown in (1.4):

$$F = \mu\, [u_{ik} - (1/3)\delta_{ik}\, u_{\ell\ell}\,]^2 + (1/2)\, K\, u_{\ell\ell}{}^2 \qquad (3.1).$$

It can be also shown that,[3]

$$\sigma_{ik} = dF/du_{ik} \qquad (3.2),$$

from which one can determine the stress tensor σ_{ik}:

$$\sigma_{ik} = 2\mu\, [u_{ik} - (1/3)\delta_{ik}\, u_{\ell\ell}] + K\, u_{\ell\ell}\, \delta_{ik} \qquad (3.3).$$

This expression determines the **stress tensor** σ_{ik} in terms of the **strain tensor** u_{ik} for an **isotropic body**.

(3.1) Homogeneous Deformations.

This is a simple case where the strain tensor is **constant** throughout the volume of the body. In this case using (4.3) and the Lamé relations

(1.6) and (1.7) we verify that the free energy per unit of volume F defined (3.1) becomes written as

$$F = [E/2(1+\nu)] \{ u_{ik}^2 + [\nu/(1-2\nu)] u_{\ell\ell}^2 \} \qquad (3.4),$$

$$\sigma_{ik} = [E/(1+\nu)] \{ u_{ik} + [\nu/(1-2\nu)] u_{\ell\ell} \delta_{ik} \} \qquad (3.5)$$

and, conversely,

$$u_{ik} = [(1+\nu) \sigma_{ik} - \nu \sigma_{\ell\ell}\delta_{ik}]/ E \qquad (3.6).$$

The total energy F_{total} is obtained integrating (3.4) over volume V of the body,

$$F_{total} = \int_V F\, dV \qquad (3.7).$$

(4) Energy of Deformed Thin Plate.

By a thin plate we mean that its thickness along z, normal to the plane (x,y), is small compared with its dimensions in the other two (x,y). The deformations themselves are supposed small, as before. In the present case the deformation is small if the displacements of points in the plate are small compared with its thickness.

Let us suppose that the displacement vector **u** for points in neutral surface (middle of the plate) is given by

$$u_x = u_y = 0 \qquad \text{and} \qquad u_z = \zeta(x,y) \qquad (4.1).$$

If there are only internal forces, that is, $F_{external} = 0$ from (1.4) we have $\partial\sigma_{ik}/\partial x_k = 0$ and the boundary condition $n_k \sigma_{ik} = 0$, where **n** is unit vector outward normal to the film surface.[3] Since the plate is only slightly deformed we can take the normal vector **n** along the z-axis. Thus, in both surfaces of the plate $\sigma_{xz} = \sigma_{yz} = \sigma_{zz} = 0$. As the plate is thin and they are zero on each surface these tensor components must also be zero everywhere in the plate. We can therefore equate them to zero and use this condition to determine the components of the strain tensor. Thus, from the general formulae (3.5) we have

$$\sigma_{zx} = [E/(1+\nu)] u_{zx}, \qquad \sigma_{zy} = [E/(1+\nu)] u_{zy}$$

and

$$\sigma_{zz} = [E/(1+\nu)(1-2\nu)] \{ (1-\nu)u_{zz} + \nu(u_{xx} + u_{yy}) \} \qquad (4.2).$$

Equating these expressions to zero,[3] we obtain $\partial u_x/\partial z = - \partial u_z/\partial x$, $\partial u_y/\partial z = - \partial u_z/\partial y$, $u_{zz} = -\nu(u_{xx} + u_{yy})/(1-\nu)$. In the first two of these equations the component u_z can, with good accuracy, be replaced by $\zeta(x,y)$:

$$\partial u_x/\partial z = - \partial\zeta/\partial x, \qquad \partial u_y/\partial z = - \partial\zeta/\partial y, \quad \text{whence}$$

$$u_x = -z(\partial\zeta/\partial x) \qquad \text{and} \qquad u_y = -z(\partial\zeta/\partial y) \qquad (4.3).$$

If the function $\zeta = \zeta(x,y)$ **is known** integrating (4.3) using the boundary conditions $u_x = u_y = 0$ for $z = 0$ we can determine $u_x(x,y)$ and $u_y(x,y)$. In the next step, knowing $u_x(x,y)$ and $u_y(x,y)$ we can calculate all components of the **strain tensor** u_{ik} taking into account that

$$u_{xx} = -z(\partial^2\zeta/\partial x^2) \quad , \quad u_{yy} = -z(\partial^2\zeta/\partial y^2) \quad , \qquad u_{xy} = - z(\partial^2\zeta/\partial x\partial y),$$

$$u_{xz} = u_{yz} = 0 \qquad \text{and} \qquad u_{zz} = z\,[\nu/(1-\nu)]\,(\partial^2\zeta/\partial x^2 + \partial^2\zeta/\partial y^2) \qquad (4.4).$$

Now we can calculate the free energy per unit of volume of the plate using the general formula (3.4). A simple calculation gives

$$F = z^2[E/(1+\nu)]\{(\partial^2\zeta/\partial x^2 + \partial^2\zeta/\partial y^2)^2 + [1/2(1-\nu)][(\partial^2\zeta/\partial x\partial y)^2 - (\partial^2\zeta/\partial x^2)(\partial^2\zeta/\partial y^2)]\} \quad (4.5)$$

The total free energy of the plate F_{plate} is obtained by integrating over the volume of the plate. The integration over z is from -t/2 to +t/2, where t is the plate thickness, and (x,y) over the surface of the plate. So, the total energy $F_{plate} = \int F\,dV = \int F dxdydz$ of the deformed plate is, with $dA = dx\,dy$,

$$F_{plate} = [Et^3/24(1-\nu^2)]\iint[(\partial^2\zeta/\partial x^2 + \partial^2\zeta/\partial y^2)^2 + 2(1-\nu)\{(\partial^2\zeta/\partial x\partial y)^2 - (\partial^2\zeta/\partial x^2)(\partial^2\zeta/\partial y^2)\}]dA \quad (4.5).$$

(5) One Dimensional Thin Film Wrinkling.

In Fig.2 a **rigid film** (f) is deposited on a **soft elastic substrate**(s). This rigid film attached to a soft elastic medium creates a large number of waves, wrinkles, on the system film & substrate. This wrinkling is a result of a compression of the film(see Fig.2).

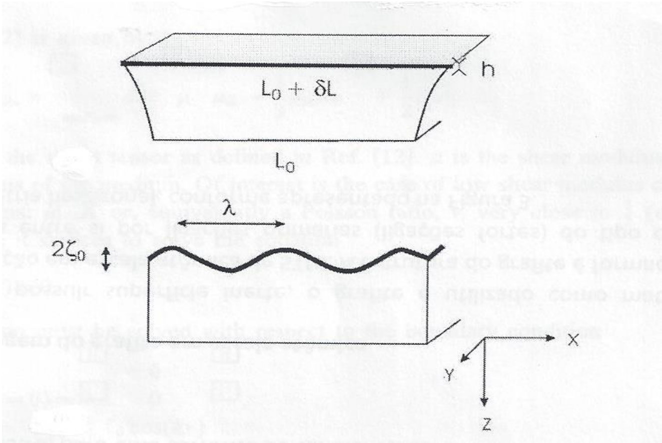

Figura 2. Strain release of a film (f) connected to the soft substratum(s): in the upper side we see the film before the release. In lower side is seen after the release when the wrinkled state emerges with wavelength λ and an amplitude ζ_o.

(5.1) Elastic Energy of the Deformed Film.

To estimate the elastic free energy F_f of the wrinkled rigid film with thickness t we suppose that the film deformation $\zeta(\mathbf{r}) = \mathbf{u}(x,y)$, in the z-direction is given by

$$\zeta(\mathbf{r}) = \zeta_o \cos(kx) \qquad (5.1),$$

where $k = 2\pi/\lambda$, are pure cosine deformation in the x-direction and where $\zeta_o << t$. In this way (4.5) becomes written as

$$F_f = [E_f t^3/24(1-\nu_f^2)] \int d^2\mathbf{r}\, |\mathrm{lapl}(\zeta(\mathbf{r}))|^2 \qquad (5.2),$$

where E_f and ν_f are, the Young modulus E_f and Poisson ratio of the film, respectively.[3,6] The integral is done over the (x,y) plane of the film; the deformation is such that no stretching of the film is required.[3,6] The amplitude of the deformation ζ_o is also assumed to be much smaller that the wavelength λ, that is, $\lambda >> \zeta_o$. Inserting (5.1) in (5.2) and performing the integration over the (x,y) plane we get

$$F_f/A = [E_f t^3/48(1-\nu_f^2)]\, \zeta_o^{\,2} k^4 \qquad (5.3),$$

where A is film area. In Fig.2 is shown the film attached to a substrate (s) deformed by the wrinkle of the film (f).

(5.2) Elastic Energy of the Deformed Substrate.

The elastic energy F_s of the deformed substrate in terms of the deformations $\mathbf{u}(x,y,z)$ is given by (3.7): [3,6]

$$F_s = \int_V d^3\mathbf{r}\,\Big[\mu_s\,(u_{ik} - \delta_{ik}\,u_{\ell\ell}/3)^2 \;+\; K_s\,u_{\ell\ell}^{\;2}/2\Big] \qquad (5.4),$$

where the integration is done in the substrate volume V. Of interest is the case of low shear modulus $\boldsymbol{\mu_s = G_s}$ compared to bulk modulus $K_s = E_s$, that is, $K_s >> \mu_s$ or, equivalently a Poisson ratio $\nu \sim 1/2$ typical of *elastomers*. In this case using (3.5) we have $\sigma_{ik} = K_s u_{\ell\ell}\,\delta_{ik}$ showing that only diagonal terms σ_{ik} contribute, that is, $\sigma_{ii} = 3K_s u_{ii}$. As there is no external forces from (3.3) we have $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$, resulting $u_{\ell\ell} = 0$, that is,

$$\mathrm{div}(\mathbf{u}) = 0 \qquad (5.5).$$

This equation must be solved with respect to the boundary conditions $\mathbf{u}(x, z = 0) = [0 , 0, \zeta_o \cos(kx)]$, i.e. the surface of the medium must match the wrinkle of the plane given by (5.1). Very far from the film the deformation must be zero: $\mathbf{u}(x, z \to\infty) = 0$. Solving (5.5) submitted to the above boundary conditions we have

$$\mathbf{u}(x,y,z) = [\, kz\sin(kx) , 0 , (1+kz)\cos(kx)]\, \zeta_o \exp(-kz) \qquad (5.6).$$

Inserting (5.6) in (5.4) we obtain[6]

$$F_s/A = G_s\, k\, \zeta_o^{\,2}/2 \qquad (5.7).$$

The wrinkle has emerged in the film due to the interaction between the **film** and **substrate**. We add the plate energy given by (5.3) with film energy given by (5.7) to obtain the total energy F_{tot} of the system:

$$F_{tot} = F_f/A \;+\; F_s/A = [E_f\, t^3/48(1- \nu_f^{\,2})]\, \zeta_o^{\;2}\, k^4 \;+\; G_s\, k\, \zeta_o^{\,2}/2 \qquad (5.8).$$

It is clear that there is an optimum wavelength λ that minimizes the total F_{tot} free energy. Large wavelengths (low k) are not favorable due to the large deformations of the **substrate**, whereas the short λ are too costly due to the bending of a **rigid** film.[6] From minimization of (5.8) with respect to k it is found that the optimum (**1-direction wavelength**) λ_{1d} is given by

$$\lambda_{1d} = 2\pi t \eta_{1d}^{\;1/3} \qquad (5.9),$$

where

$$\eta_{1d} = E_f/12G_s\,(1- \nu_f^{\,2}) \qquad (5.10).$$

Taking into account the Lame relation (1.7) $G = E/2(1+\nu)$ we get

$$\eta_{1d} = [(1+\nu_s)/6\,(1-\nu_f^2)]\,(E_f/E_s) \qquad (5.11)$$

Thus, using (5.9) and (5.11) we verify that the 1-dimensional wrinkling wavelengths λ_{1d} are given by

$$\lambda_{1d} = 2\pi t\, C_{sf}\,(E_f/E_s)^{1/3} \qquad (5.12),$$

where the parameter $C_{sf} = [(1+\nu_s)/6\,(1-\nu_f^2)]^{1/3}$.

Let us take, for instance, $t = t^*\,10^{-9}$ m, $\lambda = \lambda^*\,10^{-6}$ m, $E_f = e_f\,10^9$ Pa and $E_s = \epsilon_s\,10^6$ Pa $= \epsilon_s$ MPa. In this way, defining $R = (\lambda^*/2\pi t^* C_{sf})$ we get from (5.12)

$$\epsilon_s = 10^{-2}\,e_f/R^3 \qquad (5.13).$$

A simple estimation of (5.13) can be done putting $\nu_s \approx \nu_f \approx 0.3$, $t^* \approx 2$, $\lambda^* \approx 5$ getting $R^3 \sim 0.3$ and, consequently, $\epsilon_s \sim 3.33\,10^{-2}\,e_f$. In this way, if $E_f \sim 80$ GPa, that is, $e_f = 80$ we see that $\epsilon_s \sim 2.6$, which implies that $E_s \sim 2.4$ MPa. This value is compatible with measured Young polyurethane elastic modulus.[7]

(6) Isotropic Thin Film Wrinkling.

Supposing that instead of a **1-dimensional** wrinkling, analyzed above, there is an **isotropic wrinkling,** the parameter η_{1d} would be replaced by η_{iso}:[6]

$$\eta_{iso} = \{(3-4\nu_s)/(1-\nu_s)\}\,\eta_{1d} \qquad (6.1),$$

In this way instead of (5.9) we have now

$$\lambda_{iso} = 2\pi t\, C_{sf}(iso)\,[E_f/E_s]^{1/3} \qquad (6.2),$$

where $C_{sf}(iso) = [(3-4\nu_s)\,(1+\nu_s)/6(1-\nu_s)(1-\nu_f^2)]^{1/3}$.

(7) Experimental and Theoretical Results.

In this section our theoretical prediction are compared with the experimental results of Fernanda et al.[8] shown in Fig.3.In this experiment the wrinkling wavelengths have been measured when DLC films are deposited on PDMS substrates previously exposed to oxygen plasma.

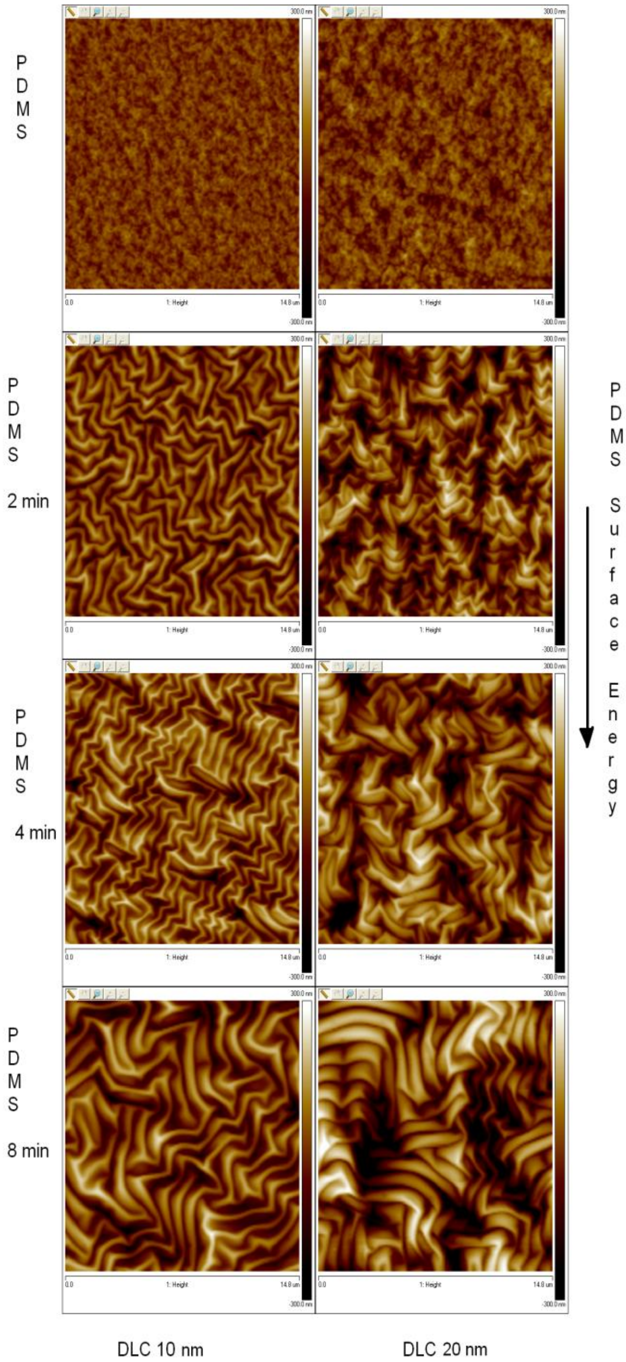

Figure 3. Wrinkling wavelengths measured in reference [8].

The measured wavelengths λ for $t = 19.5$ nm with $E_f = 75.8$ GPa are,

$$\lambda(t) = 2.200,\ \ 3.460,\ \ 5.870\ \text{ and }\ 11.680.\ \text{(nm)} \qquad (7.1)$$

and for $t = 10.8$ nm with $E_f = 192$ GPa are

$$\lambda(t) = 1.660,\ \ 2.600,\ \ 3.520\ \text{ and }\ 4.560.\ \text{(nm)} \qquad (7.2).$$

(7.1) One-dimensional Wrinkling**.**

For $t = 19.5$ nm we verify, using (5.12) and (5.13), that E_s measured in MPa would be given, respectively, by 4.4, 1.1, 0.2 and 0.03. Showing a fair agreement between theory and experiment. For $t = 10.8$ nm we verify, using (5.12 and (5.13), that E_s measured in MPa would be given, respectively, by 4.4, 1.1, 0.4 and 0.2. Showing a fair agreement between theory and experiment.

(7.2) Isotropic Wrinkling.

Putting $\nu_s \approx \nu_f \approx 0.3$ we verify that $C_{sf}(iso) \sim 1.6\ C_{sf}(1d)$ implying that $\lambda_{iso} \sim 1.6\ \lambda_{1d}$ .This shows that the wavelengths of **isotropic wrinkles** would be about 2 times larger than the **1-dimensional** ones.

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