c) The Exact Fresnel Formalism (Optical Treatment)

Born approximation diverges for $q_z \to 0$ $\Rightarrow$

The reflected intensity **cannot** be larger than the incident intensity.
Multiple scattering for small angles have to be taken into account.

Starting point: Helmholtz equation
(remember: neutrons can be treated as waves)

$$\nabla^2 \boldsymbol{E}(\boldsymbol{r}) + k_0^2 n^2(\boldsymbol{r})\, \boldsymbol{E}(\boldsymbol{r}) = 0$$

$\boldsymbol{r}$: vector in space
$\boldsymbol{E}$: electrical field for photons / wave function for neutrons
$k_0 = 2\pi/\lambda$: modulus of the wave vector
n : refractive index **for reflectivity :** $n(\boldsymbol{r}) = n(z)$

Electron density (for x-rays) or scattering length density (neutrons) translates to the refractive index :

$$n(z) = 1-\delta(z)+i\beta(z)$$

with the dispersion δ and the absorption β.

X-rays:

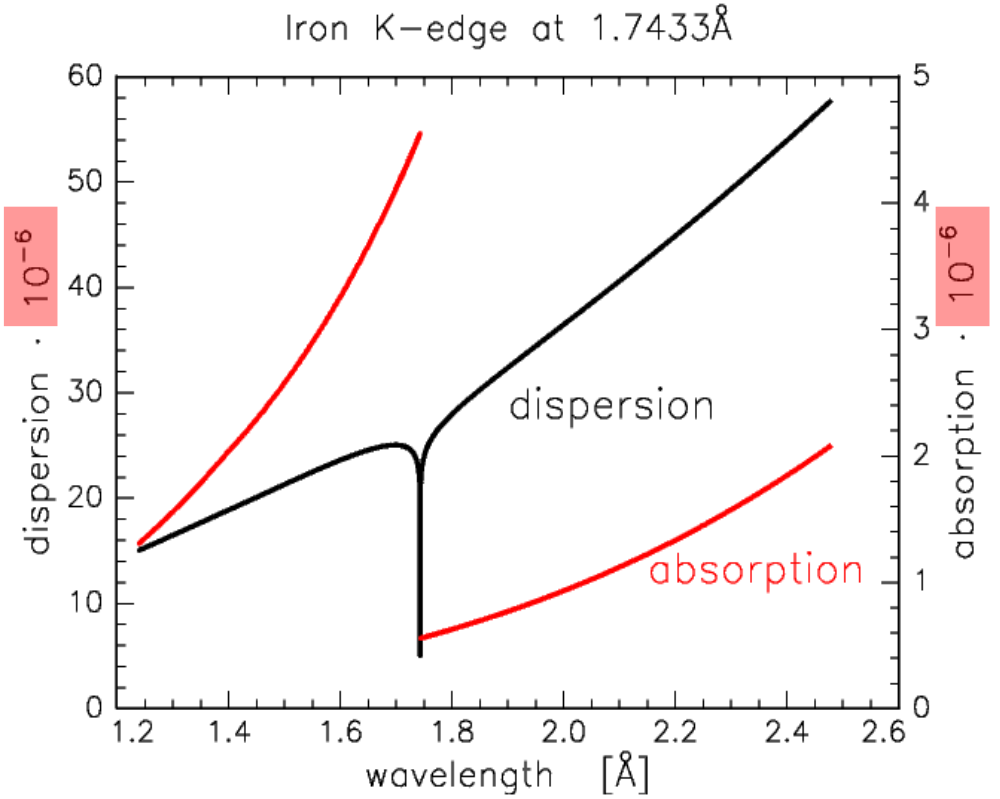
$$\delta(z)=\frac{\lambda^2}{2\pi} r_e \rho(z) \frac{f_0(q_z)+f_{\Re}(\lambda)}{Z}$$

$$\beta(z)=\frac{\lambda^2}{2\pi} r_e \rho(z) \frac{f_{\Im}(\lambda)}{Z}$$

r_e : classical e⁻ radius ρ : e⁻ density

Z : number of e⁻ f_0 : formfactor

$f_{\Re} + i\, f_{\Im}$: corrections to formfactor



Neutrons:

$$\delta(z)=\frac{\lambda^2}{2\pi} N(z) b$$

β is usually negligible

N : particle density

b : scattering length

Mean value of the refractive index: $n<1$

$\Rightarrow$ total external reflection

$\Rightarrow$ critical angle α_c

$$\alpha_c \approx \sqrt{2\delta}$$

Fresnel reflection coefficient for a single smooth surface:

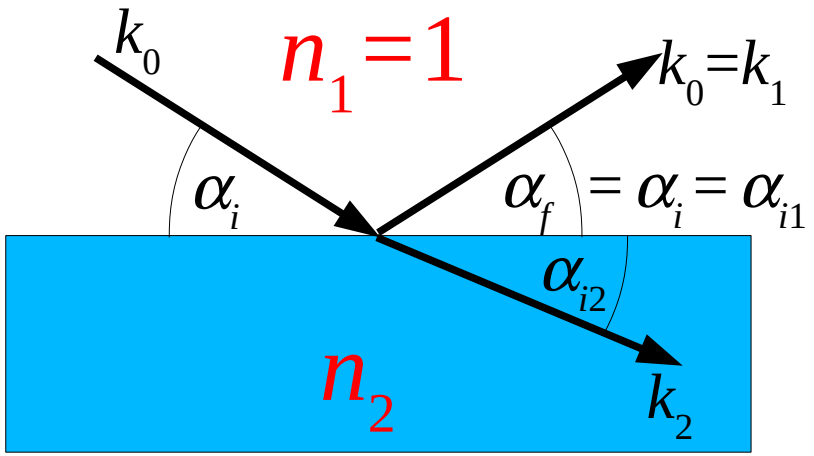
$$r_{1,2} = \frac{k_{z1} - k_{z2}}{k_{z1} + k_{z2}}$$

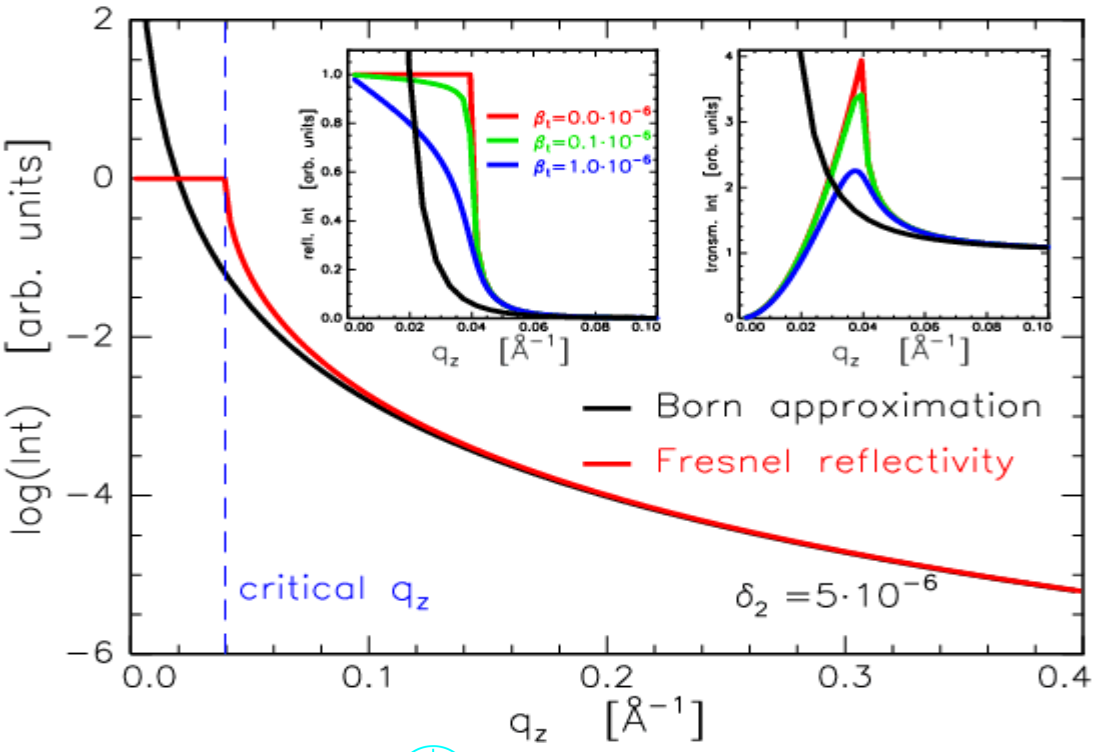
with

$$k_{z1} = k_1 \sin\alpha_{i1} = k_0 \sin\alpha_i = q_z/2$$

$$k_{z2} = k_2 \sin\alpha_{i2} = k_0 \sqrt{n_2^2 - \cos^2\alpha_i}$$

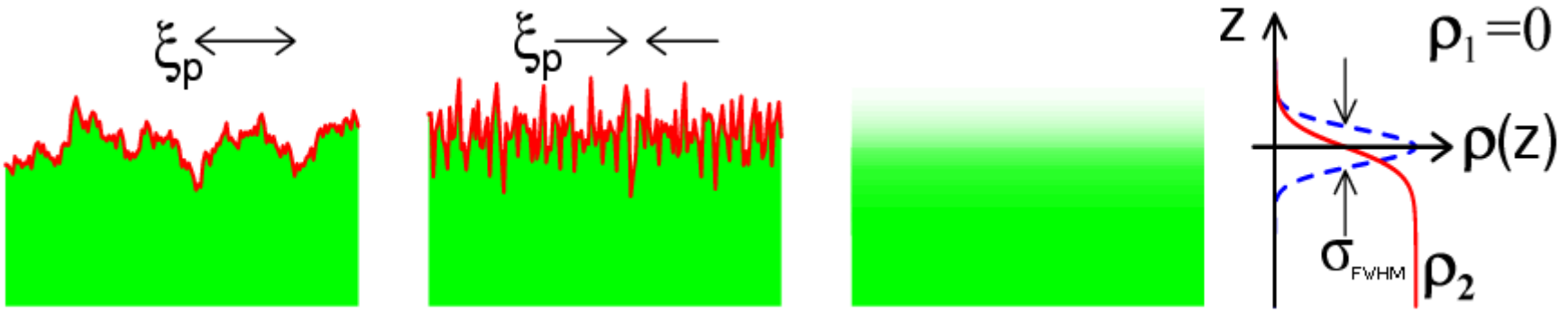
$$I(\alpha_i) = |r_{1,2}|^2$$





If a surface is rough, the Fresnel reflection coefficient can be modified.

The result depends on the exact probability function of the interface.



Solids : Error-function profile $\Rightarrow$ Gaussian probability function

Polymers : tanh-function profile $\Rightarrow$ $1/\cosh^2$ probability function

$$\tilde{r}_{1,2} = r_{1,2} \exp\left(-2 k_{z1} k_{z2} \sigma^2\right)$$

Gaussian

$$\tilde{r}_{1,2} = \frac{\sinh\left[\sqrt{3}\,\sigma\left(k_{z1} - k_{z2}\right)\right]}{\sinh\left[\sqrt{3}\,\sigma\left(k_{z1} + k_{z2}\right)\right]}$$

$1/\cosh^2$

Smooth layer systems (recursive formalism by Parratt)

for each interface j : $r_{j,j+1} = \frac{k_{z,j} - k_{z,j+1}}{k_{z,j} + k_{z,j+1}}$ $k_{z,j} = k_0 \sqrt{n_j^2 - \cos^2 \alpha_i}$

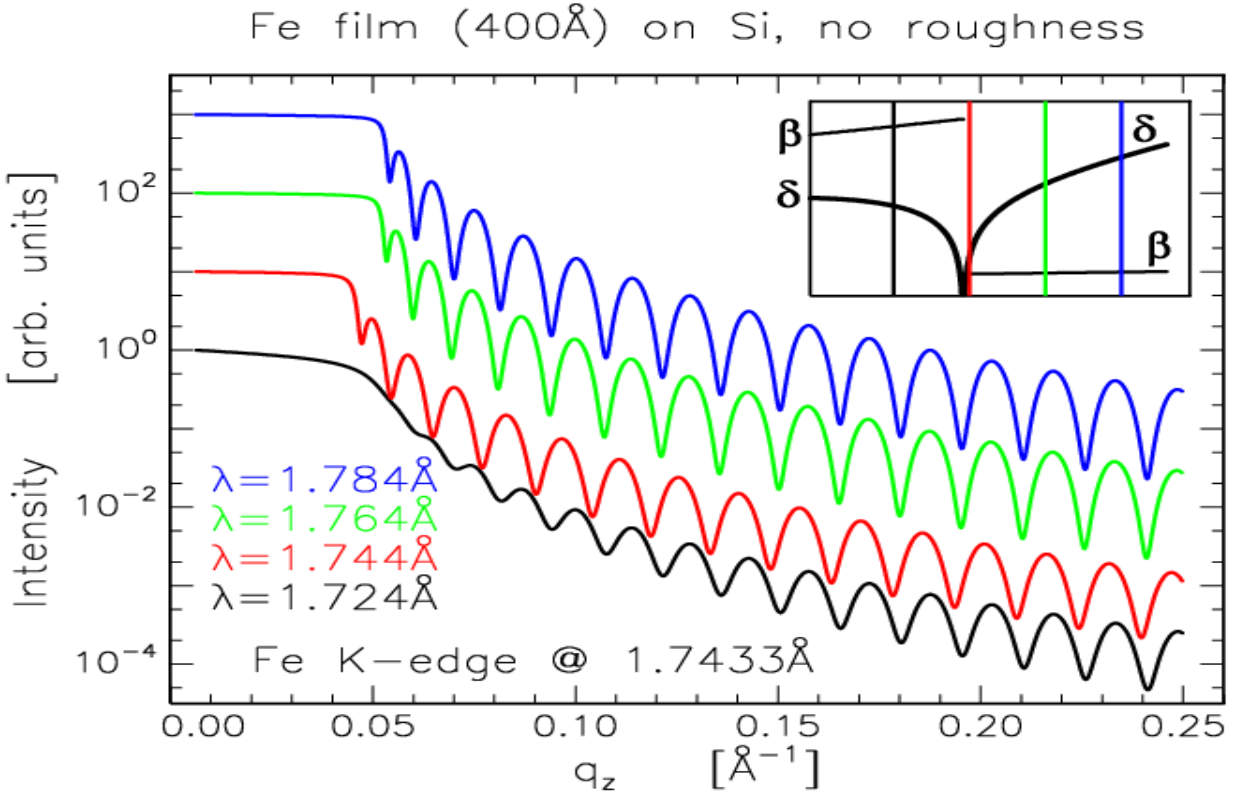
Recursion:

starting with $X_{N+1} = 0$

(N : number of layers)

end of recursion:

$$|X_1|^2 = I(q_z)$$



$$X_j = \exp(-2ik_{z,j} z_j) \frac{r_{j,j+1} + X_{j+1} \exp(2ik_{z,j+1} z_j)}{1 + r_{j,j+1} X_{j+1} \exp(2ik_{z,j+1} z_j)}$$

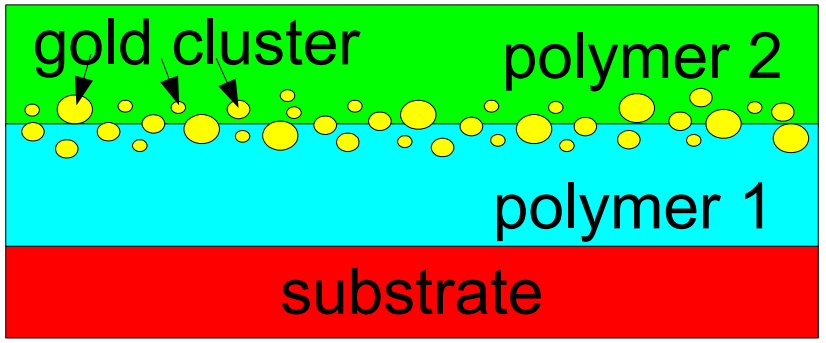
For rough layer systems the $r_{j,j+1}$ can be replaced by the $\tilde{r}_{j,j+1}$

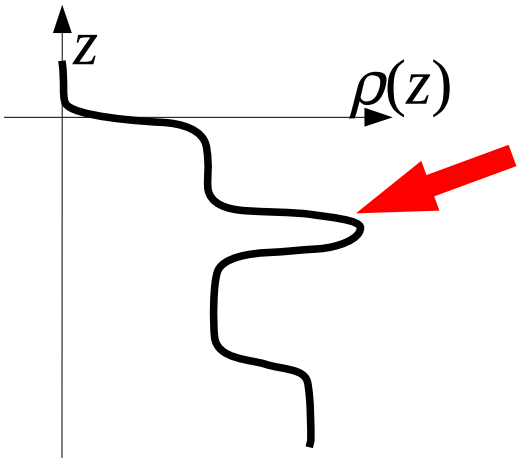
$$\tilde{X}_j = \exp\left(-2ik_{z,j}z_j\right)\frac{\tilde{r}_{j,j+1} + X_{j+1}\exp\left(2ik_{z,j+1}z_j\right)}{1+\tilde{r}_{j,j+1}X_{j+1}\exp\left(2ik_{z,j+1}z_j\right)}$$

However, this is only an approximation.

It fails for thin layers with large roughness.

e.g.

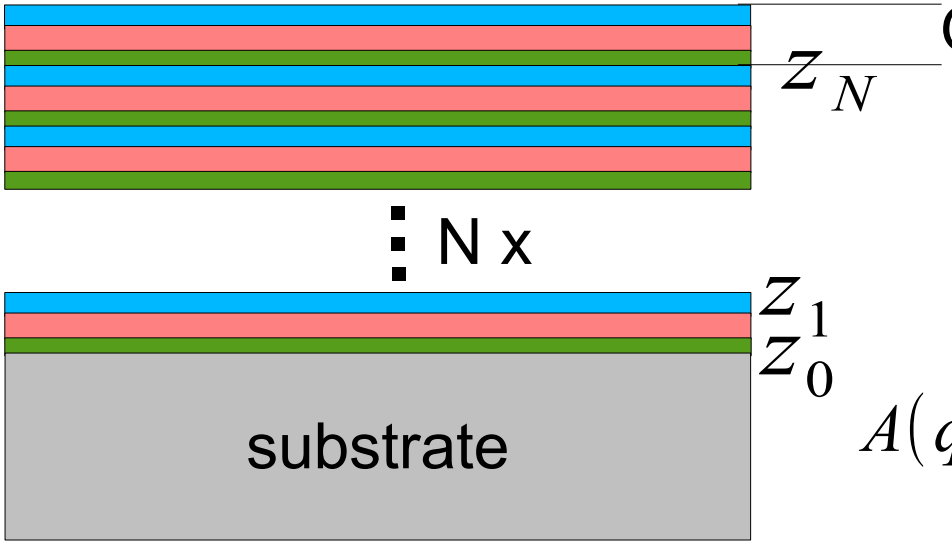




This layer can be described by a standard thin film model but the Parratt formalism may fail.

There is a way to get around this problem (see later).

Multilayer systems



One sub-unit with thickness $d7$

Amplitude in Born approximation

$$A(q_z) \propto \frac{1}{q_z^2}\int \frac{d\rho(z)}{dz}\exp(iq_z z)\,dz$$

If all sub-units are identical:

$$\begin{aligned} A(q_z) &\propto \frac{1}{q_z^2}\int\left(\sum_{n=1}^{N}\frac{d\rho_u(z)}{dz}\exp(iq_z z_n)\right)\exp(iq_z z)\,dz \\ &\propto \frac{1}{q_z^2}\sum_{n=1}^{N}\left(\int\frac{d\rho_u(z)}{dz}\exp(iq_z z)\,dz\right)\exp(iq_z z_n) \\ &\propto \frac{1}{q_z^2}\left(\int\frac{d\rho_u(z)}{dz}\exp(iq_z z)\,dz\right)\sum_{n=1}^{N}\exp(iq_z z_n) = \frac{1}{q_z^2}F(q_z)S(q_z) \end{aligned}$$

Form factor

$$F(q_z) = \int \frac{d\,\rho_u(z)}{dz} \exp(iq_z z)\, dz$$

Structure factor

$$S(q_z) = \sum_{n=1}^{N} \exp(iq_z z_n) = \sum_{n=1}^{N} \exp(iq_z \cdot nd) \propto \frac{\sin(Nq_z d/2)}{\sin(q_z d/2)}$$

Form factor contains the information about the sub-unit

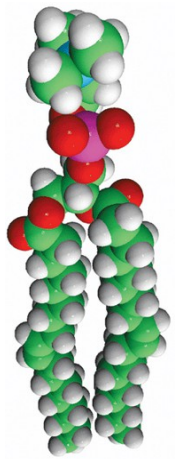
Structure factor contains the information about the repetition

The sub-unit and the repetition are decoupled in Born approximation

Example

DOCP

1,2-Dioleoyl-sn-glycero-3-phosphocholine



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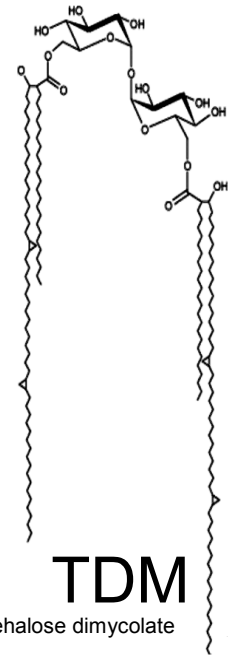
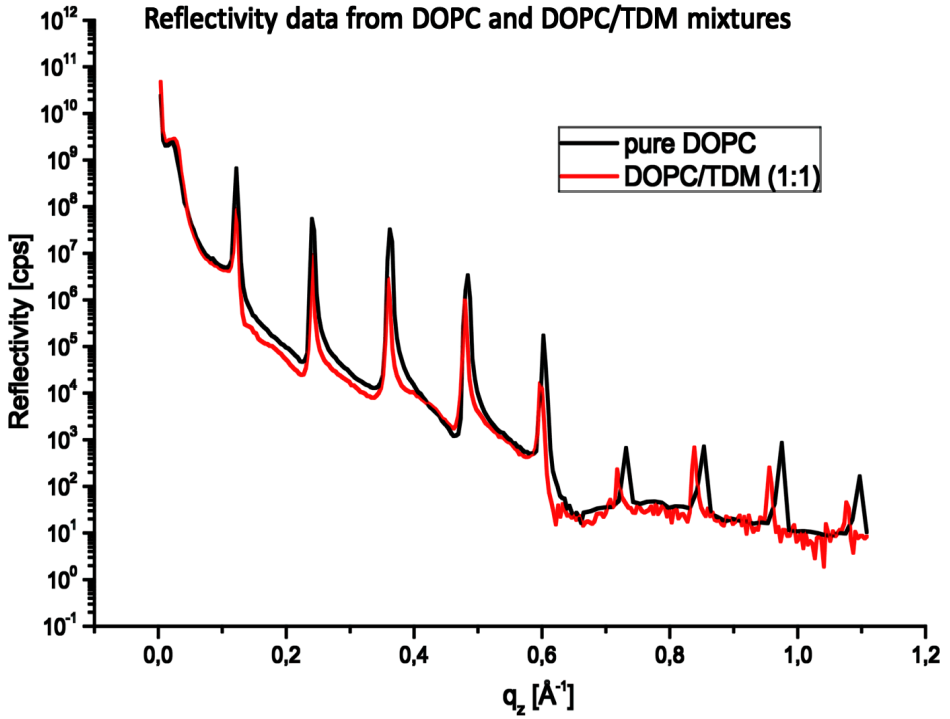


TDM

Trehalose dimycolate

from tubercolosis bacteria

=>



Gutsmann, Beerlink et al.

Multilayer systems (dynamical scattering)

Abelès or transfer matrix method (equivalent to Parratt)

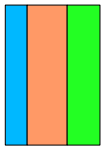
A characteristic matrix for each layer with layer thickness d_j exists

$$M_j = \begin{pmatrix} \exp(ik_{z,j}d_j) & r_{j,j+1}\exp(ik_{z,j}d_j) \\ r_{j,j+1}\exp(-ik_{z,j}d_j) & \exp(-ik_{z,j}d_j) \end{pmatrix}$$

For a layer system $$M = \prod_{j=0}^{N} M_j$$

The resulting reflectivity is $$I(q_z) = \left| \frac{M_{2,1}}{M_{2,2}} \right|^2$$

For large number of repetitions computing time can be much smaller than for Parratt:

e.g.: x 8  ....

Parratt : 3 x 8 = 24 iterations

Abelès : $M_{lay} = M_{\blacksquare} \cdot M_{\blacksquare} \cdot M_{\blacksquare}$, $M_2 = M_{lay} \cdot M_{lay}$

$M_4 = M_2 \cdot M_2$, $M_8 = M_4 \cdot M_4$

5 multiplications