

van der Waals interactions across stratified media

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Working at the Lifshitz level, we investigate the van der Waals interactions across a series of layers with a periodic motif. We derive the complete form of the van der Waals interaction as an explicit function of the number of periodic layers. We then compare our result with an approximation based on an anisotropic-continuum representation of the stratified medium. Satisfactory agreement between discrete-layer and continuum models is reached only for thicknesses of ten or more layers.

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I. INTRODUCTION

Once one starts looking for them, multilayers are everywhere. (Bio)macromolecules such as phospholipid layers¹ are prone to create multilamellar assemblies either in solution or in apposition to supporting interfaces.² Layer upon layer of polymer multilayers, assembled either electrostatically³ or through interlayer hydrogen bonding,⁴ allow the fabrication of multicomposite molecular assemblies of tailored architecture⁵ with important technological applications. Understanding molecular interactions in these systems is an important step in controlling the assembly process. Though these interactions are due to many different specific processes, the van der Waals interactions are their common feature. Unless one is satisfied with the pairwise additive formulation of van der Waals interactions in multilayer geometries,⁶ their general and exact derivation on the Lifshitz level is complicated, abstruse, and seldom attempted.

Here we will set up a new approach to the van der Waals–Lifshitz interactions in multilayer geometries based on a recent reformulation of the Lifshitz theory⁷ in terms of an algebra of 2×2 matrices that allows us to derive simple

and transparent formulas for the van der Waals interactions across finely layered systems. We use this reformulation to evaluate the interactions across a multilayer and then compare these with a continuum uniaxial-dielectric approximation based on van der Waals interactions across anisotropic media.

II. FORMALISM

We consider a symmetric periodic array, Fig. 1, between a leftmost half-space L and a rightmost half-space R . The periodic motif is the sequence of AB pairs repeated N times between L and R , schematically $LABAB \cdots ABAR$.

Recently, we showed⁷ that in the Lifshitz theory, a computation of the secular determinant of the electromagnetic field modes can be mapped onto an algebra of 2×2 matrices. The secular determinant, in fact, follows from the 11 element of a transfer matrix that can be simply constructed from the interaction geometry as a product of discontinuity \mathbb{D} and propagator \mathbb{T} matrices. In the case considered here, following the “mnemonic” introduced in Ref. 7, the transfer matrix assumes the form

$$M = \underbrace{D_{RA} \times T_A \times D_{AB} \times T_B \times D_{BA}}_A \times \cdots \times \underbrace{T_A \times D_{AB} \times T_B \times D_{BA}}_A \times T_A \times D_{AL}. \quad (1)$$

In this notation the discontinuity and the propagator matrices become

$$D_{AB} = \begin{pmatrix} 1 & -\bar{\Delta} \\ -\bar{\Delta} & 1 \end{pmatrix} = -D_{BA}, \quad (2)$$

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and

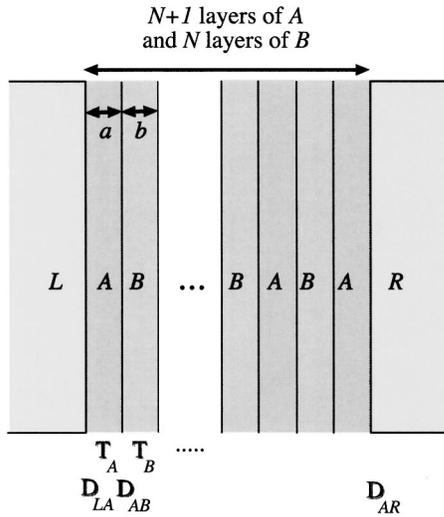


FIG. 1. The symmetric periodic array between a leftmost region L and a rightmost region R . The periodic motif is the AB pair of layers repeated N times between L and R , symbolically $LABAB \dots ABAR = L(AB)^N AR$. The thickness of layer A (hydrocarbon) is a , and that of layer B is b (water). Matrices D_{LA} , D_{AB} , D_{AR} , and $T_{A,B}$ are defined in the main text.

$$T_{A,B} = \begin{pmatrix} 1 & 0 \\ 0 & e^{-2\rho_{A,B}a,b} \end{pmatrix}, \quad (3)$$

where a and b are the thicknesses of the A and B regions, and

$$\bar{\Delta} = \left(\frac{\rho_A \epsilon_B - \rho_B \epsilon_A}{\rho_A \epsilon_B + \rho_B \epsilon_A} \right), \quad (4)$$

with $\epsilon_A(\omega)$ and $\epsilon_B(\omega)$ the frequency-dependent dielectric functions of regions A and B . Finally,

$$A^N = \frac{(\det A)^{N/2}}{\sinh \xi} \begin{pmatrix} \sinh N\xi \frac{a_{11}}{\sqrt{\det A}} - \sinh(N-1)\xi & \sinh N\xi \frac{a_{12}}{\sqrt{\det A}} \\ \sinh N\xi \frac{a_{12}}{\sqrt{\det A}} & \sinh N\xi \frac{a_{11}}{\sqrt{\det A}} - \sinh(N-1)\xi \end{pmatrix}, \quad (9)$$

where

$$\xi \equiv \log \frac{1}{2} \frac{\text{Tr } A}{\sqrt{\det A}} \left(1 + \sqrt{1 - 4 \frac{\det A}{(\text{Tr } A)^2}} \right). \quad (10)$$

Here e^ξ and $e^{-\xi}$ are the two eigenvalues of the unitary matrix $A^* = A/\sqrt{\det A}$, viz., for unitary matrices the product of the eigenvalues equals one. From the definition of ξ , Eq. (10), we derive explicitly

$$\begin{aligned} \xi &= (\rho_A a + \rho_B b) - \log \frac{u}{1 + \sqrt{1 - (u e^{-(\rho_A a + \rho_B b)})^2}} \\ &= (\rho_A a + \rho_B b) - \log f(u, \rho_A a + \rho_B b), \end{aligned} \quad (11)$$

$$\rho_{A,B}^2 = Q^2 - \frac{\epsilon_{A,B} \omega^2}{c^2}. \quad (5)$$

We will assume that region A corresponds to hydrocarbon, $\epsilon_A(\omega)$, and regions L, B, R to water, $\epsilon_B(\omega)$, dielectric response. We use the standard^{12,13} forms for $\epsilon_A(\omega)$ and $\epsilon_B(\omega)$, where the dielectric response of water is described with one microwave relaxation frequency, five infrared relaxation frequencies and six ultraviolet relaxation frequencies and that of the hydrocarbons with four relaxation frequencies.

The discontinuity matrix describes the propagation of the electromagnetic modes across the dielectric boundary and the propagator matrix their propagation inside a dielectrically homogeneous region. The above equations are strictly valid for the transverse magnetic (TM) field modes.¹¹ The result appropriate for the transverse electric (TE) field modes¹¹ is obtained analogously, *via* a formal substitution,

$$\bar{\Delta} = \left(\frac{\rho_A \epsilon_B - \rho_B \epsilon_A}{\rho_A \epsilon_B + \rho_B \epsilon_A} \right) \rightarrow \Delta = \left(\frac{\rho_A \mu_B - \rho_B \mu_A}{\rho_A \mu_B + \rho_B \mu_A} \right), \quad (6)$$

where $\mu_{A,B}$ are the magnetic permeabilities of the regions A, B . The transfer matrix can be written equivalently in the form

$$M = D_{RA} \times A^N \times T_A \times D_{AL}, \quad (7)$$

where the matrix A can be obtained as

$$\begin{aligned} A &= T_A \times D_{AB} \times T_B \times D_{BA} \\ &= \begin{pmatrix} 1 - \bar{\Delta}^2 e^{-2\rho_B b} & \bar{\Delta}(1 - e^{-2\rho_B b}) \\ -\bar{\Delta} e^{-2\rho_A a} (1 - e^{-2\rho_B b}) & e^{-2\rho_A a} (e^{-2\rho_B b} - \bar{\Delta}^2) \end{pmatrix}. \end{aligned} \quad (8)$$

The product A^N can be factored via the Abelés formula for square matrices.⁸ This formula can be reproduced straightforwardly *via* induction, starting from the trivial $N=2$ case,⁹ so that

where we defined

$$u = \frac{2(1 - \bar{\Delta}^2)}{1 - \bar{\Delta}^2 (e^{-\rho_A a} + e^{-\rho_B b}) + e^{-2(\rho_A a + \rho_B b)}}$$

and

$$f(u, \rho_A a + \rho_B b) = \frac{u}{1 + \sqrt{1 - (u e^{-(\rho_A a + \rho_B b)})^2}}. \quad (12)$$

The product A^N can be further decomposed as

$$A^N = \frac{(\det A)^{N/2} e^{(N-1)\xi}}{(1 - e^{-2\xi})} P, \quad (13)$$

where

$$P(N) = \begin{pmatrix} p_{11}(N) & p_{12}(N) \\ p_{21}(N) & p_{22}(N) \end{pmatrix} \\ = (1 - e^{-2N\xi}) \frac{A}{\sqrt{\det A}} - e^{-\xi} (1 - e^{-2(N-1)\xi}) I, \quad (14)$$

with the unit matrix I .

In Lifshitz theory the fluctuation free energy is directly related to the 11 elements of the transfer matrix M ;⁷ here

$$m_{11} = \frac{(\det A)^{N/2} e^{(N-1)\xi}}{(1 - e^{-2\xi})} (p_{11}(N) + p_{21}(N) \bar{\Delta}_{RA} \\ + e^{-2\rho_A a} \bar{\Delta}_{AL} (p_{12}(N) + p_{22}(N) \bar{\Delta}_{RA})). \quad (15)$$

The mode equation, or the secular determinant of the TM field modes, can be written as

$$m_{11}^{\text{TM}} = \mathcal{D}_{\text{TM}}(\omega, Q) = 0, \quad (16)$$

with an analogous equation for TE field modes.¹ The combined secular determinant thus equals the product $\mathcal{D}(\omega, Q) = \mathcal{D}_{\text{TM}}(\omega, Q) \mathcal{D}_{\text{TE}}(\omega, Q)$. The free energy of the fluctuating modes in a system of N (AB) layers can now be cast⁷ into a form containing the secular determinant of the TM and TE modes,

$$\mathcal{F}(N; a, b) = kT \sum_Q \sum_{n=0}^{\infty} \ln \mathcal{D}(i\xi_n, Q) \\ = kT \sum_Q \sum_{n=0}^{\infty} \ln m_{11}^{\text{TM}}(i\xi_n, Q) \\ + kT \sum_Q \sum_{n=0}^{\infty} \ln m_{11}^{\text{TE}}(i\xi_n, Q), \quad (17)$$

where ω has been substituted by the imaginary Matsubara frequencies $i\xi_n = i2\pi(kT/\hbar)n$ and the primed sum signifies that the $n=0$ term is taken with the weight 1/2. What we will investigate now is the dependence of the van der Waals interaction free energy, defined as the difference,

$$F(N; a, b) = \mathcal{F}(N; a, b) - \mathcal{F}(N \rightarrow \infty; a, b), \quad (18)$$

on the number of (AB) layers, N . From the above definition of the interaction free energy we obtain the corresponding Hamaker coefficient $H(N; a, b)$ as

$$F(N; a, b) = \frac{H(N; a, b)}{12\pi(a+b)^2 N^2}. \quad (19)$$

III. RESULT

We first write the 11 elements for the TM modes in a form that makes explicit the dependence on N . We first notice that

$$\log m_{11} = -\log 2 \sinh \xi + N \log \sqrt{\det A} e^{\xi} + \log(p_{11}(N) \\ + p_{21}(N) \bar{\Delta}_{RA} + e^{-2\rho_A a} \bar{\Delta}_{AL} (p_{12}(N) \\ + p_{22}(N) \bar{\Delta}_{RA})), \quad (20)$$

so that the corresponding free energy, Eq. (17), has three terms. The first does not depend on N and is thus not of immediate concern here. The second term, linear in N , represents the chemical potential or the free energy of adding a single combined layer to the system. As already formulated in Ref. 10, this chemical potential has the form

$$\mu = \log \sqrt{\det A} \lambda^{(+)}, \quad (21)$$

where $\lambda^{(+)} = e^{\xi}$ is one of the eigenvalues of the matrix A^* . However, it is the last term of Eq. (20) that describes the interactions in the multilayer composite. Using Eqs. (17) and (18) we end up with

$$F(N; a, b) = kT \sum_Q \sum_{n=0}^{\infty} \log \left(\frac{p_{11}(N) + p_{21}(N) \bar{\Delta}_{RA} + e^{-2\rho_A a} \bar{\Delta}_{AL} (p_{12}(N) + p_{22}(N) \bar{\Delta}_{RA})}{p_{11}(\infty) + p_{21}(\infty) \bar{\Delta}_{RA} + e^{-2\rho_A a} \bar{\Delta}_{AL} (p_{12}(\infty) + p_{22}(\infty) \bar{\Delta}_{RA})} \right), \quad (22)$$

the main result of this paper. It gives the complete van der Waals interaction across the stratified medium AB in a form with an explicit dependence on the number of layers N . Not excessively complicated, it allows for straightforward numerical computations.

Before analyzing Eq. (22) in detail, we verify that it has the correct limiting behavior. When $\epsilon_A = \epsilon_B$, so that $\bar{\Delta} = 0$ with $\rho_A = \rho_B = \rho$, if the stratified medium behaves homogeneously. In this case,

$$f(u, \rho_A a + \rho_B b) = 1 \quad \text{and} \quad \xi = (\rho_A a + \rho_B b) = \rho(a + b). \quad (23)$$

Furthermore, in the same limit we obtain for the matrix P ,

$$P = 2 \sinh(\rho_A a + \rho_B b) \begin{pmatrix} 1 & 0 \\ 0 & e^{-2N(\rho_A a + \rho_B b)} \end{pmatrix}. \quad (24)$$

From these, Eq. (22) becomes

$$F(N; a, b) = kT \sum_Q \sum_{n=0}^{\infty} \log(1 \\ + \bar{\Delta}_{RA} \bar{\Delta}_{AL} e^{-2\rho(a+N(a+b))}). \quad (25)$$

Thus, we recover the standard Lifshitz expression for the interaction of media L and R across the medium $A=B$ of thickness $a+N(a+b)$. Obviously, in the limit where the dielectric properties of A and B coincide, this is just the total thickness of the region A .

The general formula, Eq. (22) can be rewritten as

$$\mathbb{F}(N;a,b) = \frac{kT}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} Q dQ \log \left(\frac{p_{11}(N) + p_{21}(N) \bar{\Delta}_{RA} + e^{-2\rho_A a} \bar{\Delta}_{AL} (p_{12}(N) + p_{22}(N) \bar{\Delta}_{RA})}{p_{11}(\infty) + p_{21}(\infty) \bar{\Delta}_{RA} + e^{-2\rho_A a} \bar{\Delta}_{AL} (p_{12}(\infty) + p_{22}(\infty) \bar{\Delta}_{RA})} \right). \quad (26)$$

Its consequences can be fully appreciated only after a full numerical analysis. In Fig. 2 we evaluate the $n=0$ term separately and then compare it to the full n summation that includes retardation effects, Fig. 3.

IV. NUMERICAL COMPUTATIONS AND CONCLUSIONS

For intuition about the general result, Eq. (26), we evaluate the van der Waals interactions across a slab of material of thickness $a+N(a+b)$, the continuum composite of layers A and B of Fig. 1. Because of its layered structure, we can associate with it a transverse dielectric function $\epsilon_{\perp} = \epsilon_{xx} = \epsilon_{yy}$ and a longitudinal dielectric function $\epsilon_{\parallel} = \epsilon_{zz}$. The continuum composite is thus a uniaxial dielectric with two distinct values of the dielectric response parallel and perpendicular to the layer normal. In terms of the dielectric functions ϵ_A and ϵ_B by analogy to capacitors in series and in parallel,

$$\epsilon_{\perp} = \frac{1}{a+b} (a\epsilon_A + b\epsilon_B) \quad \text{and} \quad \frac{1}{\epsilon_{\parallel}} = \frac{1}{a+b} \left(\frac{a}{\epsilon_A} + \frac{b}{\epsilon_B} \right). \quad (27)$$

The longitudinal and the transverse dielectric response of a layered continuum composite thus depend on the volume fractions $a/(a+b)$ and $b/(a+b)$ of the materials A and B in the system.

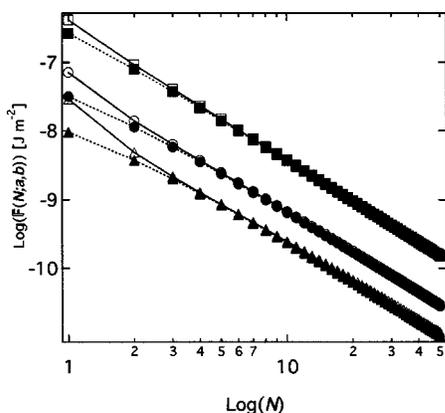


FIG. 2. Zero frequency $n=0$ van der Waals interaction free energy across a multilayered slab of layers A and layers B ; $a, b = 4$ nm (circles); $a = 1$ nm, $b = 4$ nm (triangles); $a = 8$ nm, $b = 4$ nm (squares). Region A corresponds to lipid, regions B, L, R to water with static dielectric functions (Ref. 13) $\epsilon_A = 2$ and $\epsilon_{B,L,R} = 80$. The result of the exact equation (26) (bold curves) as well as approximate anisotropic continuum model, Eq. (30) (dashed curves) are presented. Clearly the exact and the approximate results differ only for small, $N \leq 10$, number of layers.

We use the result of Šarlah and Žumer¹⁴ to derive the van der Waals interactions in a nonisotropic homogeneous uniaxial slab composed of periodic layers. If we associate the index \bar{A} with the continuum uniaxial composite, we have for the TM modes,

$$\rho_A^2 = \frac{\epsilon_{\perp}}{\epsilon_{\parallel}} \left(Q^2 - \frac{\epsilon_{\parallel} \omega^2}{c^2} \right). \quad (28)$$

The corresponding values for

$$\bar{\Delta}_{RA} = \left(\frac{\rho_A \bar{\epsilon}_A - \rho_A \epsilon_{\perp}}{\rho_A \bar{\epsilon}_A + \rho_A \epsilon_{\perp}} \right) = -\bar{\Delta}_{AL}, \quad (29)$$

and *mutatis mutandis*¹⁴ for the TE field modes. Thus, we obtain the interaction free energy as

$$\mathbb{F}(N;a,b) = \frac{kT}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} Q dQ \log \left(1 + \bar{\Delta}_{RA} \bar{\Delta}_{AL} e^{-2\rho_A (a+N(a+b))} \right), \quad (30)$$

plus an analogous term for the TE modes. This is the expression that we will compare with our exact formula, Eq. (26).

Figure 2 gives the dependence of the zeroth-order term, $n=0$, interaction free energy $\mathbb{F}(N;a,b)$, in its exact form Eq. (26) as well as its continuum approximate form, Eq. (30), on the number of layers N , where we have taken A to corre-

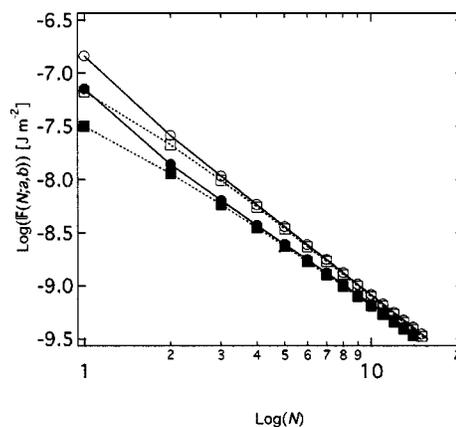


FIG. 3. The complete van der Waals interaction free energy Eq. (26) across N layers of hydrocarbon, A , and water, B , with thicknesses $a, b = 4$ nm. The exact formula for N layers, Eq. (26); open circles, bold lines for the complete n sum; open squares, dashed line for the $n=0$ term (as in Fig. 2). The approximate anisotropic continuum model, Eq. (30), with full circles, dashed lines for the complete n sum and full squares, dashed line for the $n=0$ term (same as in Fig. 2). Exact and approximate results again differ only for a small, $N \leq 10$, number of layers.

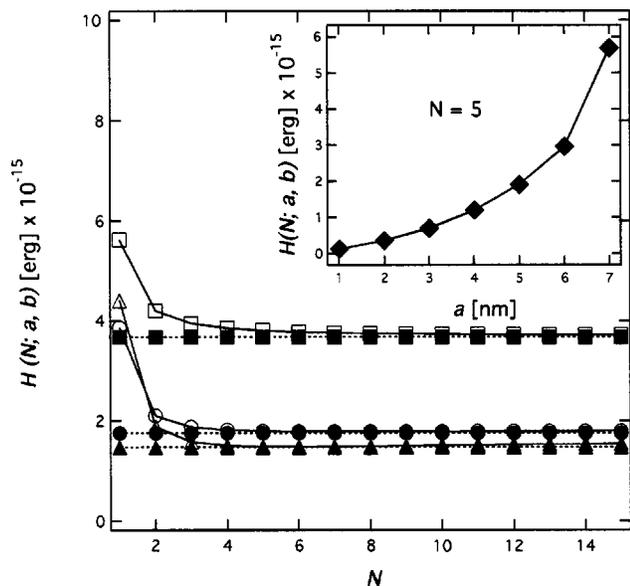


FIG. 4. The $n=0$ Hamaker coefficient, Eq. (19), of the van der Waals interaction across a multilayered slab of hydrocarbon layers A and water layers B . Here $a=1$ nm, $b=4$ nm (triangles), $a,b=4$ nm (circles), and $a=8$ nm, $b=4$ nm (squares). Depending on the dielectric properties and the volume fractions of materials A and B , the effect of the granularity persists for N on the order of 10 layers. Inset: the variation of the Hamaker coefficient at $N=5$ layers as a function of the thickness of the lipid layer, a at $a+b=8$ nm. Clearly the largest Hamaker coefficient is obtained for larger volume fractions of the lipid material.

spond to hydrocarbon and B , L , R to correspond to water. The cases for $b=4$ nm and $a=1, 4, 8$ nm are shown. It is clear from Fig. 2 that the effect of the discreteness of layers is effectively gone after about ten layers in the stack. Also, obviously, the interaction free energy is larger the larger the volume fraction of the lipid in the system.

The same is true also for the complete form, Eq. (26), with the explicit summation over n , Fig. 3. The higher-order terms in the n -summation are obviously important only for small N . In both cases, $n=0$, as well as a full summation over n , the way the continuum limit is approached obviously depends on the characteristics of the layers, especially on their respective thicknesses. As is well known¹³ for the hydrocarbon–water system, the $n=0$ term gives the dominant contribution to the interaction energy and assures that, contrary to the case of other materials, the van der Waals interactions have a nonretarded form, even at very large separations.

The $n=0$ Hamaker coefficient, Fig. 4 and Eq. (19), reinforces conclusions based on the evaluation of the interaction free energy. Again, the continuum limit of the Hamaker coefficient is safely reached after about ten layers, the swiftness of the transition to the continuum approximation being dictated by the thickness and the dielectric properties of the layers A and B . Also, the magnitude of the Hamaker coefficient, for fixed thickness of the periodic layer, $a+b=8$ nm in the case examined, depends on the volume fraction of both

layers. It is biggest when the lipid layer volume fraction is highest. This is indeed as one would expect since for high water volume fractions the dielectric inhomogeneity and thus van der Waals interactions are nonexistent. It is only at much higher values of N that the effect of retardation will set in, leading to a leveling off of the Hamaker coefficient at about half its $n=0$ value. Since our focus here is the granularity or stratification of the medium, we do not delve any further on the retardation effects.

If the Hamaker coefficient were evaluated in the model based on an isotropic mixture of A and B , it would be about 20% smaller than in the anisotropic continuum model. Also, unless the thickness of A and B are very dissimilar the pairwise summation would give quantitatively unsatisfactory results.

Taking into account the electrolyte screening of the $n=0$ Hamaker coefficient¹³ would not change our conclusions regarding the approach to the continuum anisotropic limit. It would just make the higher-order terms more important. This conclusion could be potentially affected only by a more sophisticated calculation that would take into account the electrolyte ion correlation effects on a two loop level.¹⁵

Comparing the exact dependence of the van der Waals interactions across a periodic multilayer on the number of layers with a continuum approximation based on the van der Waals interactions across a uniaxial anisotropic composite, we have been able to assess the validity of the continuum approximation and show that it indeed reduces to the properly defined limit after about ten layers. Again, this limit has to acknowledge the uniaxial continuum structure of the multilayer.

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