Hamaker coefficents for two identical anisotropic cylinder at all separations A comparison of Gecko Hamaker and Python results

J. Hopkins

Dan sent some data, I made A's. He generated A's from GH. I plotted both results for comparison. They should agree. They don't.

I. IMAGINARY PART OF THE DIELECTRIC RESPONSE FUNCTION AND ANISOTROPY METRIC

The dielectric response of the two dielectrically uniaxial half-spaces is given by the values of their dielectric functions $\overline{\epsilon_{\parallel}}$, parallel and $\overline{\epsilon_{\perp}}$, perpendicular to their respective axes. We shall use $\overline{\epsilon_{1,\parallel}}$ ($\overline{\epsilon_{1,\perp}}$) and $\overline{\epsilon_{2,\parallel}}$ ($\overline{\epsilon_{2,\perp}}$) for the left and right half-spaces, respectively.

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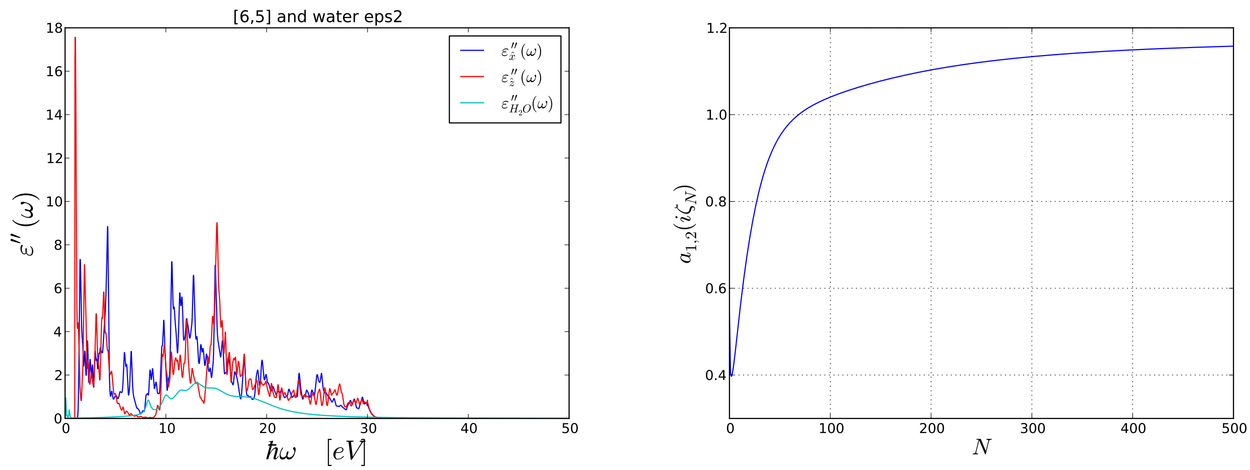

(a) (b)

FIG. 1: Full result using Eqs.7,8 (a) Anisotropic response functions for CG-10 DNA and water. The DNA response functions in the x and y directions were used as perpendicular and parallel inputs, respectively. CG-10 and water eps2 data was provided by Dan Dryden. CG-10 data scales Wai-Yim's calculations by 4.94 and is assumed to include Na (more info in Dan Dryden email sent to us on Nov. 8, 2013). Water data was built from lorentz oscillators R.H.French,J.Amer.Ceram Soc.,83,9,2117-46(2000), H.D.Ackler, et al,J.Coll.Interface Sci.179,46. (b) Anisotropy metric $a_{1,2}(i\zeta_n)$ using Eq.**??**, compares the anisotropy of the cylinders (DNA) to their intervening material, water for the terms contruting to the Matsubara sum.

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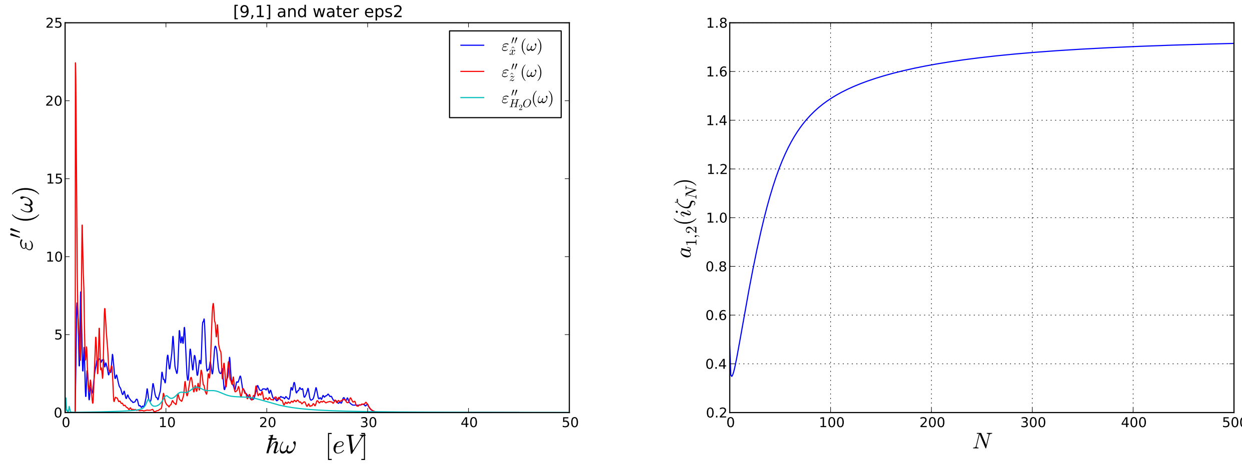

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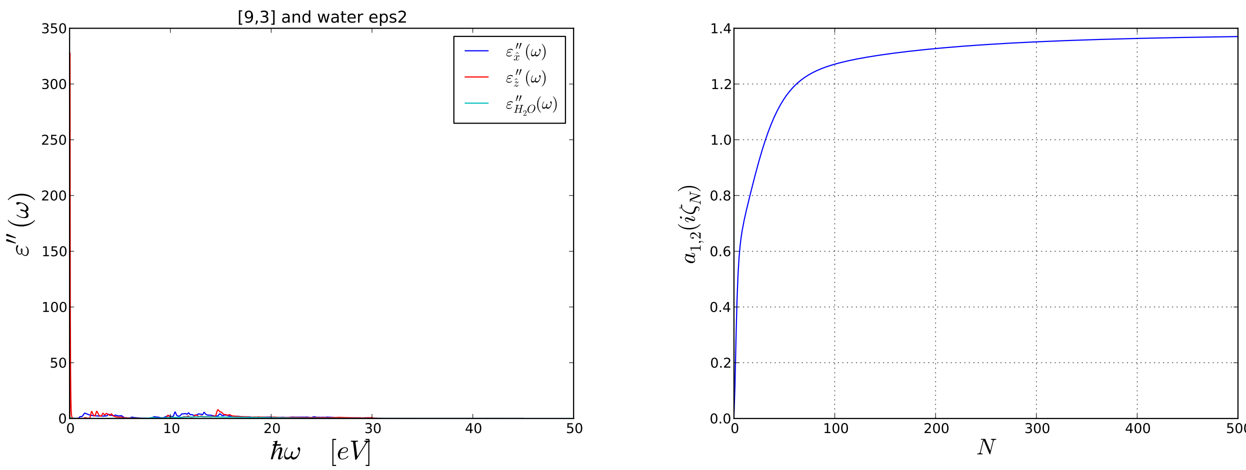

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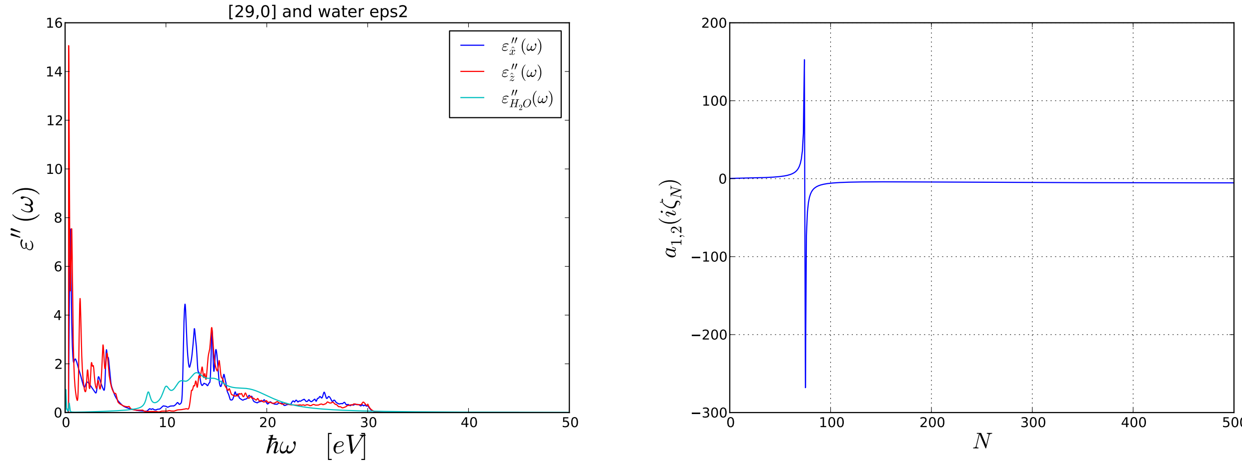

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$$\frac{d^2\mathcal{G}(\ell,\theta)}{d\ell^2} = N_1 N_2 \sin\theta \; G(\ell,\theta). \tag{1}$$

Conversely, the interaction free energy *per unit length*, $g(\ell)$, between two parallel cylinders is given by the Abel transform (see e.g. Ref. **?** , pp 233-235)

$$\frac{d^2\mathcal{G}(\ell,\theta=0)}{d\ell^2} = N_1 N_2 \int_{-\infty}^{+\infty} g(\sqrt{\ell^2+y^2})\; dy. \tag{2}$$

In both cases we expand $\mathcal{G}(\ell,\theta)$ to find the coefficient next to $v_1 v_2$ (or equivalently $N_1 N_2$), take the second derivative with respect to ℓ, then use Eqs. 1 and 2 in order to obtain the appropriate pair interaction free energy between cylinders. Note that such an expansion is possible only if the dielectric response at all frequencies is bounded. In the case of an ideal metal Drude-like dielectric response this expansion is not feasible and our method can not be transplanted to that case automatically.

II. ANISOTROPY METRIC

In order to get the interaction free energy between two anisotropic cylinders we assume that both semi-infinite substrates (half-spaces), $\mathcal{L}$ (1) and $\mathcal{R}$ (2), are composite materials made of oriented anisotropic cylinders at volume

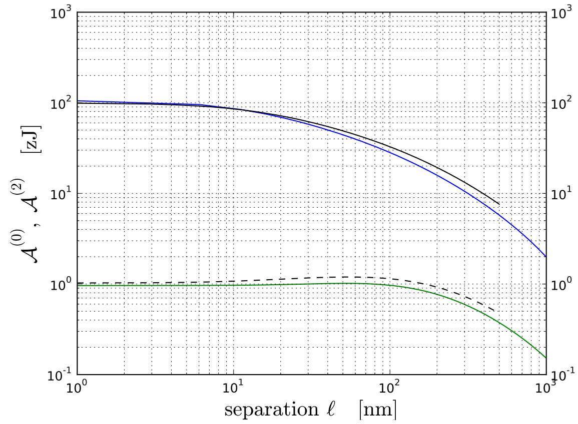


FIG. 5: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

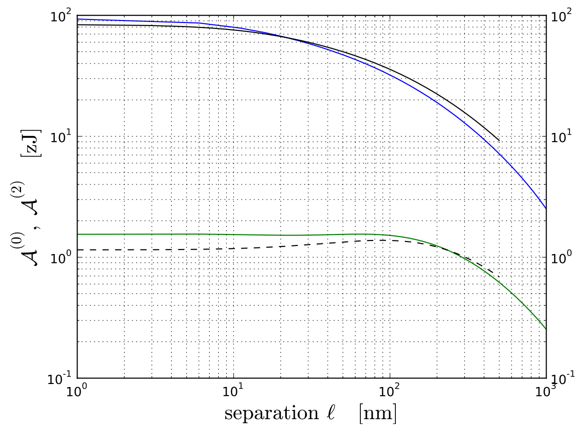


FIG. 6: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

fractions v_1 and v_2, with $\epsilon^c{}_{1,\perp}$ ($\epsilon^c{}_{2,\perp}$) and $\epsilon^c{}_{1,\parallel}$ ($\epsilon^c{}_{2,\parallel}$) as the transverse and longitudinal dielectric response functions of the cylinder materials. For the semi-infinite composite medium of oriented anisotropic cylinders with local hexagonal packing symmetry, so that the corresponding cylinder volume fraction is v, the anisotropic bulk dielectric response function can be derived in the form (see Ref. **?** , p.318)

$$\overline{\epsilon_\parallel} = \epsilon_m \left(1 + v\Delta_\parallel\right), \qquad \overline{\epsilon_\perp} = \epsilon_m \left(1 + \frac{2v\Delta_\perp}{1 - v\Delta_\perp}\right), \tag{3}$$

where the relative anisotropy measures in the parallel and perpendicular direction are given by

$$\Delta_\perp = \frac{\epsilon^c{}_\perp - \epsilon_m}{\epsilon^c{}_\perp + \epsilon_m} \qquad \Delta_\parallel = \frac{\epsilon^c{}_\parallel - \epsilon_m}{\epsilon_m}. \tag{4}$$

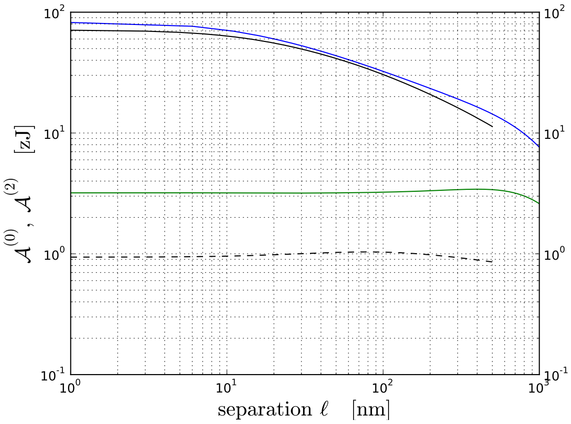


FIG. 7: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

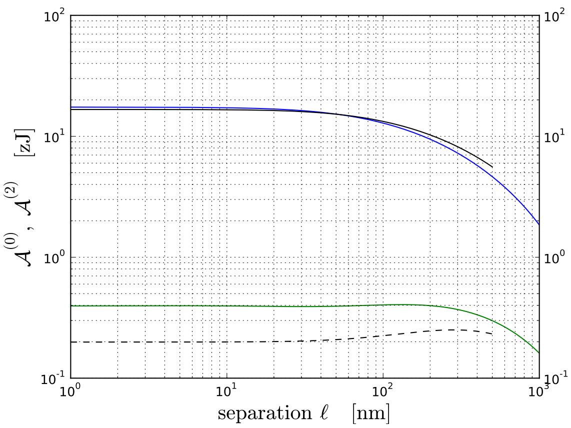


FIG. 8: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

III. PERPENDICULAR CYLINDERS

A. Fully retarded

We use Eq. 1 to obtain the interaction free energy between two skewed cylinders:

$$G(\ell,\theta) = -\frac{k_BT}{64\pi}\frac{\pi^2 R_1^2 R_2^2}{\ell^4 \sin\theta}{\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel}\int_0^\infty udu\ \frac{e^{-2\sqrt{u^2+p_n^2}}}{(u^2+p_n^2)} g(a_1,a_2,u,p_n,\theta), \tag{5}$$

where $u = Q\ell$,

$$\begin{aligned} g(a_1,a_2,u,p_n,\theta) \ &= \ 2\left[(1+3a_1)(1+3a_2)u^4 + 2(1+2a_1+2a_2+3a_1a_2)u^2p_n^2 + 2(1+a_1)(1+a_2)p_n^4\right] + \\ &\qquad + (1-a_1)(1-a_2)(u^2+2p_n^2)^2\cos 2\theta \end{aligned} \tag{6}$$

and $p_n^2(\ell) = \epsilon_m(i\omega_n)\frac{\omega_n^2}{c^2}\ell^2$. Another change of variables with $u = p_n t$, yields

$$G(\ell,\theta) = -\frac{k_BT}{64\pi}\frac{\pi^2R_1^2R_2^2}{\ell^4\sin\theta}{\sum_{n=0}^{\infty}}'\Delta_{1,\parallel}\Delta_{2,\parallel}\; p_n^4\int_0^\infty tdt\;\frac{e^{-2p_n\sqrt{t^2+1}}}{(t^2+1)}\tilde{g}(t,a_1(i\omega_n),a_2(i\omega_n),\theta), \tag{7}$$

with

$$\begin{aligned}\tilde{g}(t,a_1,a_2,\theta) \;=\; & 2\left[(1+3a_1)(1+3a_2)t^4 + 2(1+2a_1+2a_2+3a_1a_2)t^2 + 2(1+a_1)(1+a_2)\right] + \\ & + (1-a_1)(1-a_2)(t^2+2)^2\cos 2\theta. \end{aligned} \tag{8}$$

This is the final result for the cylinder-cylinder interaction at all angles when the radii of the cylinders are the smallest lengths in the system. It includes retardation and the full angular dependence. Some simple limits can be obtained form this general expression.

B. Non-retarded result

The non-retarded limit where $c \longrightarrow \infty$, has already been explored in Ref. **?** . There $p_n \longrightarrow 0$ for all n and we obtain from Eq. 5

$$\begin{aligned}G(\ell,\theta;c\longrightarrow\infty) \;=\; & -\frac{k_BT}{64\pi}\frac{\pi^2R_1^2R_2^2}{\ell^4\sin\theta}{\sum_{n=0}^{\infty}}'\Delta_{1,\parallel}\Delta_{2,\parallel}\int_0^\infty u^3du\; e^{-2u}\left[2(1+3a_1)(1+3a_2)+(1-a_1)(1-a_2)\cos 2\theta\right] = \\ =\; & -\frac{k_BT}{64\pi}\frac{\pi^2R_1^2R_2^2}{\ell^4\sin\theta}{\sum_{n=0}^{\infty}}'\Delta_{1,\parallel}\Delta_{2,\parallel}\frac{3}{8}\left[2(1+3a_1)(1+3a_2)+(1-a_1)(1-a_2)\cos 2\theta\right]. \end{aligned} \tag{9}$$

This formula could also be obtained directly from Eq. 7 taking into account that in the t integration only the terms with large t contribute to the final integral. Expanding the whole integrand for large t returns us to Eq. 9. The $n = 0$ term of this formula for two identical cylinders corresponds to classical dipolar fluctuation forces as analyzed in **?** .

IV. PARALLEL CYLINDERS

A. Fully retarded

The analysis here is somewhat more complicated because the pair interaction energy between the cylinders involves the inverse Abel transform [**?**]. We start with

$$\frac{d^2\mathcal{G}(\ell,\theta=0)}{d\ell^2} = \frac{k_BT}{2\pi}{\sum_{n=0}^{\infty}}'\int_0^\infty QdQ\frac{d^2f(\ell,\theta=0)}{d\ell^2}, \tag{10}$$

where

$$\begin{aligned}\frac{d^2f(\ell,\theta=0)}{d\ell^2} \;=\; & -\frac{v_1v_2\Delta_{1,\parallel}\Delta_{2,\parallel}}{32}\frac{e^{-2\ell\sqrt{Q^2+\epsilon_m\frac{\omega_n^2}{c^2}}}}{(Q^2+\epsilon_m\frac{\omega_n^2}{c^2})} \\ & \left\{2\left[(1+3a_1)(1+3a_2)Q^4 + 2(1+2a_1+2a_2+3a_1a_2)Q^2\epsilon_m\frac{\omega_n^2}{c^2} + 2(1+a_1)(1+a_2){\epsilon_m}^2\frac{\omega_n^4}{c^4}\right] + \right. \\ & \left. + (1-a_1)(1-a_2)(Q^2+2\epsilon_m\frac{\omega_n^2}{c^2})^2\right\}, \end{aligned} \tag{11}$$

and again $v_1 = N\,\pi R_1^2$ ($v_2 = N\,\pi R_2^2$) and $a = \frac{2\Delta_\perp}{\Delta_\parallel}$. We continue by introducing the Abel transform and its properties. Namely, if we define

$$\int_{-\infty}^{+\infty} g(\sqrt{\ell^2 + y^2})\; dy = f(y), \tag{12}$$

then

$$g(\ell) = -\frac{1}{\pi}\int_{\ell}^{+\infty} \frac{f'(y)dy}{\sqrt{y^2 - \ell^2}}. \tag{13}$$

Taking this into account when considering Eqs. 11, we remain with

$$g(\ell) = -\frac{k_BT}{32} R_1^2 R_2^2 {\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel} \int_{\ell}^{+\infty} \frac{dy}{\sqrt{y^2-\ell^2}} \int_0^{\infty} QdQ \frac{e^{-2y\sqrt{Q^2+\epsilon_m(i\omega_n)\frac{\omega_n^2}{c^2}}}}{(Q^2+\epsilon_m(i\omega_n)\frac{\omega_n^2}{c^2})^{1/2}} h(a_1(i\omega_n), a_2(i\omega_n), Q, \epsilon_m(i\omega_n)\frac{\omega_n^2}{c^2}), \tag{14}$$

where

$$\begin{aligned} h(a_1, a_2, Q, \epsilon_m \frac{\omega_n^2}{c^2}) \;&=\; 2\left[(1+3a_1)(1+3a_2)Q^4 + 2(1+2a_1+2a_2+3a_1a_2)Q^2\epsilon_m\frac{\omega_n^2}{c^2} + 2(1+a_1)(1+a_2){\epsilon_m}^2\frac{\omega_n^4}{c^4}\right] + \\ & (1-a_1)(1-a_2)(Q^2 + 2\epsilon_m\frac{\omega_n^2}{c^2})^2. \end{aligned} \tag{15}$$

As before, we introduce $p_n^2 = \epsilon_m(i\omega_n)\frac{\omega_n^2}{c^2}\ell^2$, $u = Q\ell$ and $y \longrightarrow y/\ell$. This allows us to rewrite the above integrals as

$$g(\ell) = -\frac{k_BT}{32}\frac{R_1^2R_2^2}{\ell^5} {\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel} \int_1^{+\infty} \frac{dy}{\sqrt{y^2-1}} \int_0^{\infty} udu\; \frac{e^{-2y\sqrt{u^2+p_n^2}}}{(u^2+p_n^2)^{1/2}}\; h(a_1(i\omega_n), a_2(i\omega_n), u, p_n^2), \tag{16}$$

and

$$\begin{aligned} h(a_1(i\omega_n), a_2(i\omega_n), u, p_n^2) \;&=\; 2\left[(1+3a_1)(1+3a_2)u^4 + 2(1+2a_1+2a_2+3a_1a_2)u^2p_n^2 + 2(1+a_1)(1+a_2)p_n^4\right] + \\ & (1-a_1)(1-a_2)(u^2+2p_n^2)^2. \end{aligned} \tag{17}$$

This is the final result for the interaction between two parallel thin cylinders at all separations and contains retardation effects explicitly. In general, the above expression can only be evaluated numerically once the dielectric spectra of component substances are known.

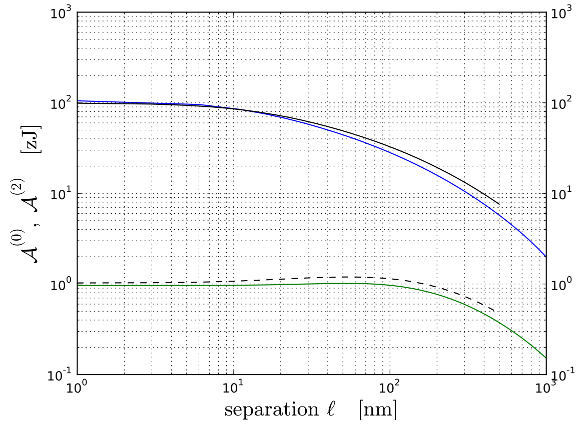
We now again transform this result into a form that is suitable for computation and numerical implementation. Rewriting Eq. 16 as

$$\boxed{g(\ell) = -\frac{3(\pi R_1^2)(\pi R_2^2)}{8\pi\;\ell^5}\mathcal{A}(\ell),} \tag{18}$$

we introduced the Hamaker coefficient

$$\mathcal{A}(\ell) = \frac{k_BT}{12\pi} {\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel} \int_1^{+\infty} \frac{dy}{\sqrt{y^2-1}} \int_0^{\infty} udu\; \frac{e^{-2y\sqrt{u^2+p_n^2(\ell)}}}{(u^2+p_n^2(\ell))^{1/2}}\; h(a_1(i\omega_n), a_2(i\omega_n), u, p_n^2(\ell)) \tag{19}$$

with $h(a_1(i\omega_n), a_2(i\omega_n), u, p_n^2(\ell))$ defined in Eq. 17. This result is simpler then in the skewed case becasue it does not contain any angle dependence. In general $\mathcal{A}(\ell)$ can not be written in terms of $\mathcal{A}^{(0)}(\ell)$ and $\mathcal{A}^{(2)}(\ell)$ of the skewed cylinders.



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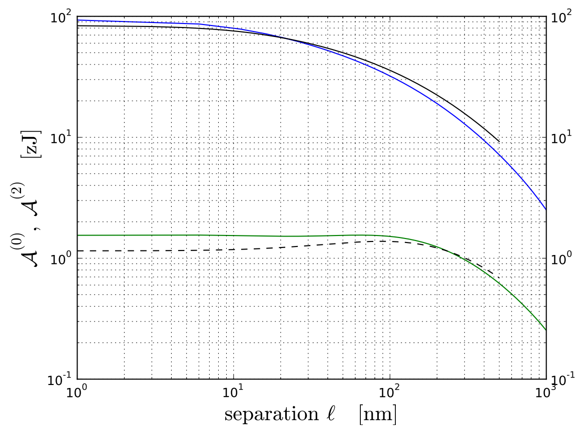

FIG. 10: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

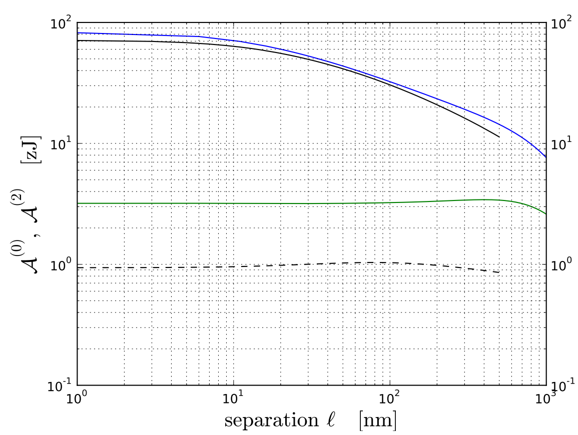

FIG. 11: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

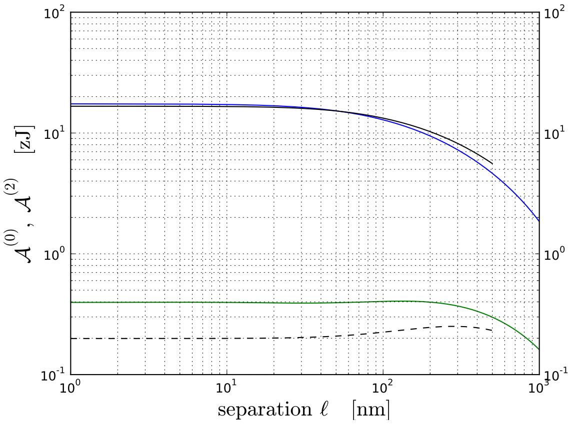

FIG. 12: A sketch of the system of interest (the two cylinders). The quantities describing the geometry of the system are denoted, together with the logitudinal and transverse directions of cylinder in the left half-space (1). The skew angle θ is about an axis normal to the planar boundary defining the limits of each half-space.

B. Non-retarded result

In the non-retarded limit, $c \longrightarrow \infty$, the above formula reduces to

$$\begin{aligned} g(\ell; c \longrightarrow \infty) &= -\frac{k_B T}{32} \frac{R_1^2 R_2^2}{\ell^5} {\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel} \left(3 + 5(a_1 + a_2) + 19 a_1 a_2\right) \int_1^{+\infty} \frac{dy}{\sqrt{y^2-1}} \int_0^{\infty} u^4 du\; e^{-2yu} = \\ & -\frac{9\; k_B T}{(64 \times 32)\pi} \frac{\pi^2 R_1^2 R_2^2}{\ell^5} {\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel} \left\{3 + 5[a_1(i\omega_n) + a_2(i\omega_n)] + 19 a_1(i\omega_n) a_2(i\omega_n)\right\}. \end{aligned} \tag{20}$$

Let us assume that the two cylinders are identical with radius a, so that we can finally write

$$\boxed{g(\ell; c \longrightarrow \infty) = -\frac{3}{(32^2)\pi} \frac{(\pi a^2)^2}{\ell^5} \mathcal{A}(\ell = 0),} \tag{21}$$

where

$$\mathcal{A}(\ell = 0) = \tfrac{3}{2} k_B T {\sum_{n=0}^{\infty}}' \Delta_{1,\parallel}\Delta_{2,\parallel} \Big(3 + 5[a_1(i\omega_n) + a_2(i\omega_n)] + 19 a_1(i\omega_n) a_2(i\omega_n)\Big) \tag{22}$$