VAN DER WAALS FORCES BETWEEN CYLINDERS

II. Retarded Interaction between Thin Isotropic Rods

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ABSTRACT We derive the retarded van der Waals interaction between two long thin parallel dielectric cylinders immersed in a solvent. The result shows that the ultraviolet interactions which may be responsible for the specificity of macromolecular interactions do not operate strongly over distances $R \geq 50$ Å. For greater distances the contribution of these frequencies ξ is damped by a factor $\propto e^{-\xi R/c}$.

1. INTRODUCTION

In a preceding paper[1] we have derived an expression for the nonretarded interaction between thin isotropic dielectric cylinders. In this paper we consider retardation of the interaction due to the finite velocity of the speed of light which become increasingly important as the separation of the interacting media increases. Their effect is to cause the interaction to decrease much more rapidly as the separation increases. For example, the interaction between planar geometries separated by a distance l changes from A/l^2 to B/l^3 due to retardation (1–3). For dipoles the interaction changes from α/l^6 to β/l^7 (4–6). This transition is not a sharp one but for most systems it takes place in the region where the separation is $\simeq 100$ Å.

For some biological systems involving cylindrical molecules, e.g. viral assembly and muscle filaments (7), this distance regime can be important and hence it is important to evaluate the retarded van der Waals force for these types of cylindrical systems.

The general formalism is given in section 2. In section 3 we restrict ourselves for simplicity to thin cylinders. Fat cylinders will be discussed elsewhere.

In section 4 we summarize our conclusions. Certain technical problems are contained in the two appendices.

2. METHOD

In order to evaluate the dispersion relation for the electromagnetic modes of interaction, we shall proceed in the following manner. First we evaluate the response of

[1] Mitchell, D. J., B. W. Ninham, and P. Richmond. 1973. *Biophys. J.* 13:359.

a single cylinder to an arbitrary incident electromagnetic wave. Then we identify this incident wave with the reflected wave of a second cylinder. The normal mode equation then follows in a straightforward manner.

Consider first then an infinite cylinder of radius a and dielectric susceptibility $\epsilon_1(\omega)$ immersed in a dielectric medium of susceptibility $\epsilon_3(\omega)$. We assume all media are nonmagnetic. The electromagnetic fields $\tilde{\mathcal{E}}$, $\tilde{\mathcal{B}}$ in the system are determined by Maxwell's equations. Taking Fourier transforms with respect to time these can be written as:

$$\nabla \times \tilde{\mathcal{E}} = i\omega\tilde{\mathcal{B}}/c \qquad \nabla \cdot \tilde{\mathcal{E}} = 0, \tag{1}$$

$$\nabla \times \tilde{\mathcal{B}} = -i\omega\tilde{\mathcal{E}}/c \qquad \nabla \cdot \tilde{\mathcal{B}} = 0.$$

From these equations we can derive the wave equations which are satisfied by the cartesian components of the fields:

$$\nabla^2\tilde{\mathcal{E}} + \frac{\omega^2\epsilon}{c^2}\tilde{\mathcal{E}} = 0, \tag{2}$$

$$\nabla^2\tilde{\mathcal{B}} + \frac{\omega^2\epsilon}{c^2}\tilde{\mathcal{B}} = 0, \tag{3}$$

where inside the cylinder $\epsilon = \epsilon_1(\omega)$ and outside $\epsilon = \epsilon_3(\omega)$. We take solutions of the form

$$\tilde{\mathcal{E}} = E\, e^{ikz},\ \tilde{\mathcal{B}} = B\, e^{ikz}, \tag{4}$$

where the z axis is parallel to the cylinder axis. The general solution to Eqs. 1–4 inside the cylinder can then be written (see Appendix I) as follows:

$$E_z = \sum_n A_n \frac{J_n(u_1 r)\, e^{in\theta}}{J_n(u_1 a)}, \tag{5}$$

$$B_z = \sum_n B_n \frac{J_n(u_1 r)\, e^{in\theta}}{J_n(u_1 a)}, \tag{6}$$

$$E_r = \frac{1}{u_1}\sum_n \left\{A_n\, ik\, \frac{J_n'(u_1 r)}{J_n(u_1 a)} - B_n \frac{n\omega}{c u_1 r}\frac{J_n(u_1 r)}{J_n(u_1 a)}\right\} e^{in\theta}, \tag{7}$$

$$E_\theta = \frac{i}{u_1}\sum_n \left\{A_n \frac{ikn}{u_1 r}\frac{J_n(u_1 r)}{J_n(u_1 a)} - B_n \frac{\omega}{c}\frac{J_n'(u_1 r)}{J_n(u_1 a)}\right\} e^{in\theta}, \tag{8}$$

where

$$u_1^2 = \frac{\omega^2\epsilon_1}{c^2} - k^2. \tag{9}$$

The subscripts z, r, θ denote the usual vector components in cylindrical coordinates, J_n are ordinary Bessel functions, and the sums over n range from $-\infty$ to ∞. The remaining components of B can be determined from Eqs. 1. Similarly, the corresponding solutions outside the cylinder are given by:

$$E_z = \sum_n \left\{ C_n \frac{H_n^{(1)}(u_3 r)}{H_n^{(1)}(u_3 a)} + F_n \frac{J_n(u_3 r)}{J_n(u_3 a)} \right\} e^{in\theta}, \quad (10)$$

$$B_z = \sum_n \left\{ D_n \frac{H_n^{(1)}(u_3 r)}{H_n^{(1)}(u_3 a)} + G_n \frac{J_n(u_3 r)}{J_n(u_3 a)} \right\} e^{in\theta}, \quad (11)$$

$$E_r = \frac{1}{u_3} \sum_n \left\{ C_n ik \frac{H_n^{(1)\prime}(u_3 r)}{H_n^{(1)}(u_3 a)} - \frac{D_n \omega n}{c u_3 r} \frac{H_n^{(1)}(u_3 r)}{H_n^{(1)}(u_3 a)} + F_n ik \frac{J_n'(u_3 r)}{J_n(u_3 a)} - \frac{G_n \omega n}{c u_3 r} \frac{J_n(u_3 r)}{J_n(u_3 a)} \right\} e^{in\theta}, \quad (12)$$

$$E_\theta = \frac{i}{u_3} \sum_n \left\{ C_n \frac{ikn}{u_3 r} \frac{H_n^{(1)}(u_3 r)}{H_n^{(1)}(u_3 a)} - D_n \frac{\omega}{c} \frac{H_n^{(1)\prime}(u_3 r)}{H_n^{(1)}(u_3 a)} + F_n \frac{ikn}{u_3 r} \frac{J_n(u_3 r)}{J_n(u_3 a)} - G_n \frac{\omega}{c} \frac{J_n'(u_3 r)}{J_n(u_3 a)} \right\} e^{in\theta}. \quad (13)$$

Here $H_n^{(1)}$ are Hankel functions of the first kind in standard notation. The coefficients F_n and G_n determine the incident wave, while the coefficients C_n and D_n determine the reflected wave, i.e., the external response to the incident wave. All these coefficients are related via the boundary conditions which are that E_z, B_z, E_θ, and $\epsilon\ E_r$ are are continuous across a boundary. These yield the following equations:

$$A_n = C_n + F_n,$$
$$B_n = D_n + G_n, \quad (14)$$

$$\frac{ikn}{u_1^2 a} A - \frac{\omega}{u_1 c} \frac{J_n'(u_1 a)}{J_n(u_1 a)} B_n = \frac{ikn}{u_3^2 a} C_n - \frac{\omega}{u_3 c} \frac{H_n^{(1)\prime}(u_3 a)}{H_n^{(1)}(u_3 a)} D_n + \frac{ikn}{u_3^2 a} F_n - \frac{\omega}{u_3 c} \frac{J_n'(u_3 a)}{J_n(u_3 a)} G_n, \quad (15)$$

$$\epsilon_1 \left[\frac{ik}{u_1} \frac{J_n'(u_1 a)}{J_n(u_1 a)} A_n - \frac{\omega n}{u_1^2 ca} B_n \right] = \epsilon_3 \left[\frac{ik}{u_3} \frac{H_n^{(1)\prime}(u_3 a)}{H_n^{(1)}(u_3 a)} C_n - \frac{\omega n}{u_3^2 ca} D_n + \frac{ik}{u_3} \frac{J_n'(u_3 a)}{J_n(u_3 a)} F_n - \frac{\omega n}{u_3^2 ca} G_n \right]. \quad (16)$$

We now eliminate A_n and B_n from Eqs. 15 and 16 using Eqs. 14. It is then straightforward to solve the resulting equations for C_n and D_n in terms of F_n and G_n. Carrying out the required algebra we obtain the relations

$$C_n = A_n^{11} F_n + A_n^{12} G_n, \tag{17}$$

$$D_n = A_n^{21} F_n + A_n^{22} G_n, \tag{18}$$

where

$$A_n^{11} = \frac{\beta'\gamma - \beta\gamma'}{\beta'\alpha - \alpha'\beta}, \tag{19}$$

$$A_n^{12} = \frac{\beta'\delta - \beta\delta'}{\beta'\alpha - \beta\alpha'}, \tag{20}$$

$$A_n^{21} = \frac{\alpha'\gamma - \alpha\gamma'}{\alpha'\beta - \alpha\beta'}, \tag{21}$$

$$A_n^{22} = \frac{\alpha'\delta - \alpha\delta'}{\alpha'\beta - \alpha\beta'}, \tag{22}$$

and

$$\alpha = -\gamma = \frac{ikn}{a}\left\{\frac{1}{u_1^2} - \frac{1}{u_3^2}\right\}, \tag{23}$$

$$\beta' = -\delta' = \frac{\omega n}{ca}\left\{\frac{\epsilon_3}{u_3^2} - \frac{\epsilon_1}{u_1^2}\right\}, \tag{24}$$

$$\beta = \frac{\omega}{c}\left\{\frac{H_n^{(1)\prime}(u_3 a)}{u_3 H_n^{(1)}(u_3 a)} - \frac{J'_n(u_1 a)}{u_1 J_n(u_1 a)}\right\}, \tag{25}$$

$$\delta = \frac{\omega}{c}\left\{\frac{J'_n(u_1 a)}{u_1 J_n(u_1 a)} - \frac{J'_n(u_3 a)}{u_3 J_n(u_3 a)}\right\}, \tag{26}$$

$$\alpha' = ik\left\{\frac{\epsilon_1}{u_1}\frac{J'_n(u_1 a)}{J_n(u_1 a)} - \frac{\epsilon_3}{u_3}\frac{H_n^{(1)\prime}(u_3 a)}{H_n^{(1)}(u_3 a)}\right\}, \tag{27}$$

$$\gamma' = ik\left\{\frac{\epsilon_3}{u_3}\frac{J'_n(u_3 a)}{J_n(u_3 a)} - \frac{\epsilon_1}{u_1}\frac{J'_n(u_1 a)}{J_n(u_1 a)}\right\}. \tag{28}$$

Eqs. 14 and 17–28 completely determine the response of a single cylinder of radius a to an arbitrary incident electromagnetic wave.

We now identify this arbitrary incident wave with a reflected wave from a second cylinder. This second cylinder is taken to be parallel to the first and is distance R from the first. Suppose that the second cylinder has radius b and dielectric susceptibility $\epsilon_2 = \epsilon_2(\omega)$. We choose a second cylindrical coordinate system (r_2, θ_2, z_2) with axis z_2 along the axis. It is clear that the z components of the *reflected* fields for the second cylinder can be written

$$E_z = \sum_n C'_n \frac{H_n^{(1)}(u_3 r_2)}{H_n^{(1)}(u_3 b)} e^{in\theta_2}, \tag{29}$$

$$B_z = \sum_n D'_n \frac{H_n^{(1)}(u_3 r_2)}{H_n^{(1)}(u_3 b)} e^{in\theta_2}. \tag{30}$$

We must now identify these fields with the incident waves for the first cylinder. This can be done if we note the addition formula for Hankel functions (8)

$$H_n^{(1)}(u_3 r_2)\, e^{in\theta_2} = \sum_{m=-\infty}^{\infty} H_{m+n}^{(1)}(u_3 R)\, J_m(u_3 r)\, e^{im\theta}. \tag{31}$$

Then the electric field given by Eq. 29 can be written as

$$E_z = \sum_m \frac{J_m(u_3 r)}{J_m(u_3 a)} J_m(u_3 a) \sum_n C'_n \frac{H_{m+n}^{(1)}(u_3 R)}{H_n^{(1)}(u_3 b)} e^{im\theta}. \tag{32}$$

We can now identify the coefficient of $e^{im\theta}$ with the coefficient F_m which occurs in Eq. 10. Thus

$$F_m = J_m(u_3 a) \sum_n C'_n \frac{H_{m+n}^{(1)}(u_3 R)}{H_n^{(1)}(u_3 b)}. \tag{33}$$

Similarly, from Eq. 30 we can relate the coefficients D'_m to the G_m of Eq. 11 using Eqs. 30 and 31:

$$G_m = J_m(u_3 a) \sum_n D'_n \frac{H_{m+n}^{(1)}(u_3 R)}{H_n^{(1)}(u_3 b)}. \tag{34}$$

From Eqs. 17, 18, 33, and 34 we deduce that

$$C_m = \sum_n A_m^{11} A_{mn} C'_n + \sum_n A_m^{12} A_{mn} D'_n, \tag{35}$$

$$D_m = \sum_n A_m^{21} A_{mn} C'_n + \sum_n A_m^{22} A_{mn} D'_n, \tag{36}$$

where

$$A_{mm} = J_m(u_3 a) \frac{H_{m+n}^{(1)}(u_3 R)}{H_n^{(1)}(u_3 b)}. \tag{37}$$

These equations can be written in a more compact form if we introduce a column vector

$$\tilde{\Gamma} = \begin{pmatrix} \vdots \\ C_m \\ D_m \\ \vdots \end{pmatrix}, \tag{38}$$

and a matrix

$$\tilde{M} = \left[\begin{array}{c:c:c:c} \cdots & \cdots & \cdots & \cdots \\ \vdots & A_m^{11}\, A_{mn} & A_m^{12}\, A_{mn} & \vdots \\ \cdots & \cdots & \cdots & \cdots \\ \vdots & A_m^{21}\, A_{mn} & A_m^{22}\, A_{mn} & \vdots \\ \cdots & \cdots & \cdots & \cdots \\ \vdots & & & \vdots \end{array} \right]; \tag{39}$$

Then Eqs. 35 and 36 have the convenient form

$$\tilde{\Gamma} = \tilde{M}\, \tilde{\Gamma}'. \tag{40}$$

It should be clear that there exists a similar equation

$$\tilde{\Gamma}' = \tilde{N}\tilde{\Gamma}, \tag{41}$$

where $\tilde{N}$ is obtained from $\tilde{M}$ by replacing a by b and u_1 by u_2 where

$$u_2^2 = \frac{\omega^2 \epsilon_2}{c^2} - k^2. \tag{42}$$

Together Eqs. 40 and 41 provide a condition for consistency on the allowed normal modes responsible for the interaction. This is

$$D(\omega) = \mathrm{Det}\,|\, 1 - \tilde{M}\tilde{N} \,| = 0. \tag{43}$$

In terms of this dispersion relation the free energy of interaction is given by the usual expression (6, 9, 10)

$$F(a, b, R) = \frac{kT}{2\pi} \int_0^\infty dk \sum_{n=0}^{\infty}{}' \ln D(i\xi_n); \qquad \xi_n = 2\pi nkT/h. \tag{44}$$

3. DISPERSION RELATION FOR THIN CYLINDERS

The expression obtained in the previous section for the dispersion relation and hence the force solves the problem completely in principle. In practice of course, Eq. 44 is quite useless unless it is reduced to a less intractable form. In this section we specialize to the case of "thin" cylinders $a, b \ll R$, (or "fat" cylinders far apart). We consider this case for two reasons: (*a*) the problem can be done, and (*b*) we have in mind subsequent applications to the energies of interaction of linear polyelectrolytes like DNA. For that problem the nature and magnitude of retardation effects, which presumably have some bearing on the specificity of interactions, are not immediately obvious from a consideration of planar interactions (1, 11, 12).

In order to carry out the required reductions, we proceed by a method similar to that developed in our previous study of the nonretarded forces between cylinders.[1] We note first that for $\xi/c,\ k < 1/R$ then $|u_3(i\xi, k)R| < 1$, and since $a, b \ll R$ we can expand the Bessel functions which occur in the matrix M in ascending powers of the arguments. This procedure yields

$$M_{mn}^{\alpha\beta} \simeq \frac{a^m b^m}{R^{m+n}} \frac{(m+n-1)!}{m!(n-1)!} < \frac{a^m b^n}{R^{m+n}} 2^{m+n}. \qquad (45)$$

The matrix elements decrease rapidly with increasing m and n. On the other hand, when $\xi/c,\ k > 1/R$ it is convenient to introduce the real positive variable

$$v_\alpha = \left\{k^2 + \frac{\xi^2 \epsilon_\alpha}{c^2}\right\}^{1/2}, \qquad (46)$$

such that

$$u_\alpha^2 = (e^{i\pi/2} v_\alpha)^2. \qquad (47)$$

Then since

$$H_n^{(1)}\,(z e^{i\pi/2}) = -\frac{2i}{\pi} e^{-in\pi/2} K_n(z) \quad -\pi < \arg z < \pi/2, \qquad (48)$$

we see from Eqs. 37, 39, and 48 that

$$M_{mn}^{\alpha\beta} \propto H_{m+n}^{(1)}(u_3 R) \propto K_{m+n}(v_3 R). \qquad (49)$$

Thus in the region $\xi/c,\ k \gg 1/R$, i.e. $|v_3 R| \ll 1$, we can use the asymptotic expansion of $K_{m+n}(z)$ to deduce that

$$M_{mn}^{\alpha\beta} \propto \frac{e^{-v_3 R}}{v_3 R}. \qquad (50)$$

Again the matrix elements decrease rapidly for all m and n. These arguments suggest that to the leading order of approximation, in evaluating the matrix $\tilde{M}\tilde{N}$ we need only to retain matrix elements for $m, n = 0, \pm 1$. This expectation is borne out by a more detailed analysis.

In order to evaluate the free energy of interaction (Eq. 44) explicitly we require.

$$\ln \{\text{Det}\,|\,1 - \tilde{M}\tilde{N}\,|\} = -\text{Tr}\,\{\tilde{M}\tilde{N} + \tfrac{1}{2}\,\tilde{M}\tilde{N}\cdot\tilde{M}\tilde{N} + \cdots\}. \qquad (51)$$

It can be shown that only the leading term contributes to leading order, so that we can take

$$\ln \{\text{Det} \mid 1 - \tilde{M}\tilde{N} \mid\} \simeq -\sum_{m,j} M_{mj}N_{jm} . \tag{52}$$

In the resulting trace (Tr) we now retain only terms for which $m, j = -1, 0, +1$. Substituting Eq. 52 into Eq. 44 yields

$$F(a, b, R) \simeq -\frac{kT}{2\pi} \int_0^{\infty} dk \sum_{m=0}^{\infty}{}' \sum_{m,j=-1}^{+1} M_{mj} N_{jn} . \tag{53}$$

A further reduction can be carried out to simplify this expression still more. The dominant contributions to the integral over k and sum over frequencies ξ_n in Eq. 53 come from the region $\nu_0 R < 1$. Hence the Bessel functions of argument $u_\alpha a$, $u_\alpha b$ which occur in the matrix elements M_{mj}, N_{jm} can be expanded in powers of ua and ub. Only the leading terms contribute to leading order. Using the limiting forms (13) we find after some algebra that

$$A_n^{11} = \left(\frac{\epsilon_3}{u_3^2} - \frac{\epsilon_1}{u_1^2}\right) \frac{u_3^2}{\epsilon_1 + \epsilon_3} \qquad n \neq 0, \tag{54}$$

$$= \frac{(\epsilon_3 - \epsilon_1)}{2\epsilon_3} a^2 u_3^2 \ln (u_3 a) \qquad n = 0, \tag{55}$$

$$A^{12}_n = \frac{i\omega}{kc} \left\{\frac{\epsilon_3}{u_3^2} - \frac{\epsilon_1}{u_1^2}\right\} \frac{u_1^2}{\epsilon_1 + \epsilon_3} \qquad n \neq 0,$$

$$= 0 \qquad n = 0, \tag{56}$$

$$= \frac{ikc}{\omega} \left\{\frac{1}{u_1^2} - \frac{1}{u_3^2}\right\} \frac{\epsilon_3}{(\epsilon_1 + \epsilon_3)} u_1^2 \qquad n \neq 0,$$

$$= 0 \qquad u = 0, \tag{57}$$

$$A = -\frac{\epsilon_3}{(\epsilon_1 + \epsilon_3)} u_1^2 \left\{\frac{1}{u_1^2} - \frac{1}{u_3^2}\right\} \qquad n \neq 0,$$

$$= 0 \qquad n = 0, \tag{58}$$

$$A_{11} = abi\pi \left(\frac{u_3}{2}\right) H_2^{(1)}(u_3 R), \tag{59}$$

$$A_{01} = bi\pi \left(\frac{u_3}{2}\right) H_1^{(1)}(u_3 R), \tag{60}$$

$$A_{10} = -a \frac{i\pi}{2} \left(\frac{u_3}{2}\right) \frac{H_1^{(1)}(u_3 R)}{\ln (u_3 b)}, \tag{61}$$

$$A_{00} = -\frac{i\pi}{2}\frac{H_0^{(1)}(u_3 R)}{\ln(u_3 b)}, \tag{62}$$

$$A_{1,-1} = -abi\pi\left(\frac{u_3}{2}\right)^2 H_0^{(1)}(u_3 R). \tag{63}$$

From Eq. 37 we note also that

$$A_{11} = -A_{-1,-1}; \qquad A_{1,-1} = A_{-1,1},$$
$$A_{1,0} = A_{-1,0}; \qquad A_{0,1} = A_{0,-1}. \tag{64}$$

From Eq. 52 we find

$$\begin{aligned} \ln\{\mathrm{Det}\,|\,1 - \tilde{M}\tilde{N}\,|\} &\simeq \sum_{m,j=-1}^{+1} M_{mj}N_{jm}, \\ &= -A_{00}B_{00}A_0^{11}B_0^{11} - 2A_{01}B_{10}A_0^{11}B_1^{11} - 2A_{10}B_{01}A_1^{11}B_0^{11} \\ &\quad - 2\{A_{11}B_{11} + A_{1,-1}B_{-1,1}\} \\ &\quad \cdot \{A_1^{11}B_1^{11} + A_1^{12}B_1^{21} + A_1^{21}B_1^{12} + A_1^{22}B_1^{22}\}, \end{aligned} \tag{65}$$

where the functions B are obtained from the functions A by replacing a with b and ϵ_1 with ϵ_2. Explicitly, after substituting Eqs. 54–64 into Eq. 65 we have

$$\begin{aligned} \ln\{\mathrm{Det}\,|\,1 - \tilde{M}\tilde{N}\,|\} &= -\frac{a^2b^2}{4}\frac{(\epsilon_3 - \epsilon_1)(\epsilon_3 - \epsilon_2)}{\epsilon_3^2}\nu_3^4 K_0^2(\nu_3 R) \\ &\quad - \frac{a^2b^2}{2}\left\{\left(\frac{\epsilon_3}{\nu_3^2} - \frac{\epsilon_2}{\nu_2^2}\right)\frac{\epsilon_3 - \epsilon_1}{\epsilon_3(\epsilon_3 + \epsilon_2)} + (\epsilon_1 \to \epsilon_2)\right\}\nu_3^6 K_1^2(\nu_3 R) \\ &\quad - \frac{a^2b^2}{2}\left\{\left(\frac{\epsilon_3}{\nu_3^2} - \frac{\epsilon_1}{\nu_1^2}\right)\left(\frac{\epsilon_3}{\nu_3^2} - \frac{\epsilon_2}{\nu_2^2}\right)\frac{\nu_3^4}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)}\right. \\ &\quad + \frac{\epsilon_3^2\nu_1^2\nu_2^2}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)}\left[\frac{1}{\nu_3^2} - \frac{1}{\nu_1^2}\right]\left[\frac{1}{\nu_3^2} - \frac{1}{\nu_2^2}\right] \\ &\quad \left. + \left(\frac{\epsilon_3}{\nu_3^2} - \frac{\epsilon_1}{\nu_1^2}\right)\left(\frac{1}{\nu_3^2} - \frac{1}{\nu_2^2}\right)\frac{\epsilon_3^2\nu_1^2\nu_2^2}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)} + (\epsilon_1 \to \epsilon_2)\right\} \\ &\quad \times \{\nu_3^4[K_2^2(\nu_3 R) + K_0^2(\nu_3 R)]\}. \end{aligned} \tag{66}$$

To obtain this expression we have used the identity Eq. 48. The quantities ν_α are defined by Eq. 46.

The free energy is now given by substituting expression 66 into expression 44. To proceed it is convenient to split Eq. 66 into two regimes corresponding to high and low frequencies.

(*a*) At low frequencies: $\xi < \xi_s = c/R\sqrt{\epsilon_3}$. In this case we can simply replace

ν_α by k. The 5th, 6th, and 7th terms on the right-hand side of Eq. 66 then vanish and we obtain

$$\log^{\xi<\xi_s}\{\mathrm{Det}\,|\,1 - \tilde{M}\tilde{N}\,|\} \simeq -\frac{a^2b^2}{4}\frac{(\epsilon_3 - \epsilon_1)(\epsilon_3 - \epsilon_2)}{\epsilon_3^2}\,k^4K_0^2(kR)$$
$$-\frac{a^2b^2}{2}\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}\right)k^4\{K_2^2(kR) + K_2^2(kR)$$
$$-\frac{a^2b^2}{2}\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3}\right) + (\epsilon_1 \leftrightarrow \epsilon_2)k^4K_1^2(kR). \quad (67)$$

Substituting Eq. 67 into Eq. 44 gives the contribution of these low frequencies to the free energy. They yield a nonretarded contribution proportional to R^{-5} similar to that obtained elsewhere.[1] Thus

$$F^<(a, b, R)$$
$$= \frac{kT}{2\pi}\sum_{\xi_n<\xi_s}{}' \int_0^\infty dk\,\log^{\xi<\xi_s}[\mathrm{Det}\,|\,1 - \tilde{M}\tilde{N}\,|]$$
$$= -\frac{\pi}{2^{11}}\frac{a^2b^2}{R^5}kT\sum_{\xi_n<\xi_s}{}'\left\{27\frac{(\epsilon_3 - \epsilon_1)(\epsilon_3 - \epsilon_2)}{\epsilon_3^2}\right.$$
$$\left. + 684\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}\right) + 90\left[\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}\right) + (\epsilon_1 \leftrightarrow \epsilon_2)\right]\right\}. \quad (68)$$

(*b*) For high frequencies: $\xi > \xi_s = c/R\sqrt{\epsilon_3}$. The analysis of this case is more complicated and details are given in Appendix II. For the case where ξ_s is in the visible or near infrared, we can use the transformation $kT\sum_\xi \to \hbar/2\pi \int d\xi$ to obtain

$$F^>(a, b, R)$$
$$= \frac{\hbar}{4\pi^2}\int_0^\infty d\xi \int_{\xi_s}^\infty dk\,\log^{\xi>\xi_s}[\mathrm{Det}\,|\,1 - \tilde{M}\tilde{N}\,|],$$
$$= -\frac{a^2b^2}{4}\frac{\hbar}{2\pi^2}\left(\frac{\pi}{R}\right)^{3/2}\int_{\xi_s}^\infty d\xi e^{-2\xi\sqrt{\epsilon_3}R/c}\left(\frac{\xi\sqrt{\epsilon_3}}{c}\right)^{7/2}$$
$$\times\left[\frac{(\epsilon_3 - \epsilon_1)(\epsilon_3 - \epsilon_2)}{4\epsilon_3^2} + \left\{\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}\right) + (\epsilon_1 \leftrightarrow \epsilon_2)\right\}\frac{63}{64}\frac{c}{\xi R\sqrt{\epsilon_3}}\right.$$
$$\left. + \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}\right)\left\{1 - \frac{(23\sqrt{2} - 1)}{32}\frac{c}{\xi R\sqrt{\epsilon_3}}\right\}\right]. \quad (69)$$

The integrals in Eq. 69 can be simplified when we note that the main contribution comes from frequencies $\xi \geq \xi_s$. We can therefore replace the dielectric susceptibilities in Eq. 69 by their values at ξ_s (we denote these by ϵ_3^s etc.). It remains to evaluate integrals of the form

$$\int_{\xi_s}^{\infty} d\xi e^{-2\xi/\xi_s}\xi^n,$$

where $n = 7/2$ and $5/2$. Introducing a change of variable $x = 2\xi/\xi_s$ we can write these as

$$\frac{\xi_s^{n+1}}{2^{n+1}}\int_2^{\infty} dx e^{-x}x^n = \frac{\xi_s^{n+1}}{2^{n+1}}\Gamma(n+1;2). \tag{70}$$

Γ is an incomplete gamma function (13). Substituting Eq. 70 into Eq. 69 we finally obtain

$$\begin{aligned} F^{>}(a, b, R) = -\frac{a^2b^2hc\pi^{3/2}}{8\pi^2\sqrt{\epsilon_3^s}2^{9/2}R^6}\Bigg\{&\frac{(\epsilon_3^s - \epsilon_1^s)(\epsilon_3^s - \epsilon_2^s)}{4\epsilon_3^2} \\ &+ \left[\left(\frac{\epsilon_3^s - \epsilon_1^s}{\epsilon_3^s}\right)\left(\frac{\epsilon_3^s - \epsilon_2^s}{\epsilon_3^s + \epsilon_2^s}\right) + (\epsilon_1^s \leftrightarrow \epsilon_2^s)\right]\frac{63}{32} \\ &+ \left(\frac{\epsilon_3^s - \epsilon_1^s}{\epsilon_3^s + \epsilon_1^s}\right)\left(\frac{\epsilon_3^s - \epsilon_2^s}{\epsilon_3^s + \epsilon_2^s}\right)\left[1 - \frac{(23\sqrt{2} - 1)}{16}\right]\Bigg\}. \end{aligned} \tag{71}$$

The retarded contribution to the free energy of interaction is then proportional to R^{-6}. The total free energy of interaction is then $F(a, b, R) \approx F^{<}(a, b, R) + F^{>}(a, b, R)$.

4. SUMMARY AND CONCLUSIONS

We have derived the retarded van der Waals free energy of interaction between two long thin dielectric cylinders immersed in a solvent. In the limit $R \rightarrow 0$ the result given by Eqs. 72, 68, and 71 reduces to the nonretarded interaction derived by us elsewhere.[1,2] From expression 69, however, it is clear that as R increases, the contributions to the interaction energy from frequencies greater than ξ_s are strongly damped due to the exponential factor. This damping corresponds to distance $R \sim c/2\xi\sqrt{\epsilon_3}$. In the ultraviolet $\epsilon_3 \sim 1$ and thus a typical ultraviolet frequency $\sim 1.5 \times 10^{16}$ rad/s is damped for distance $R \gtrsim 100$ Å. It is clear that specificity in macromolecular interactions due to ultraviolet and infrared correlations will not occur until the molecules are much closer, i.e., $R \gtrsim 50$ Å. At "large" distances [$\gtrsim$0(50 Å)], the temperature-dependent entropic contribution to the free energy due to microwave fluctuations across water will dominate in biological systems (1, 11, and footnote 1).

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APPENDIX I

Inside a cylindrical region, the cartesian components of the electric field which are solutions of the wave equation, Eq. 5, can be written:

$$E_z = \sum_n A_n J_n(ur)e^{in\theta}, \tag{A 1}$$

$$E_x = \sum_n X_n J_n(ur)e^{in\theta}, \tag{A 2}$$

$$E_y = \sum_n Y_n J_n(ur)e^{in\theta}. \tag{A 3}$$

The radial and tangential components E_r, E_θ are given in terms of E_x and E_y by the usual relations

$$E_r = E_x \cos\theta + E_y \sin\theta, \tag{A 4}$$

$$E_\theta = -E_x \sin\theta + E_y \cos\theta. \tag{A 5}$$

From Eqs. A 2, A 3, and A 4 we obtain

$$E_r = \sum_n (W_n J_{n-1} + Z_n J_{n+1})e^{in\theta}, \tag{A 6}$$

where

$$W_n = ½(X_{n-1} - iY_{n-1}),$$

and

$$Z_n = ½(X_{n+1} + iY_{n+1}).$$

From Eqs. A 2, A 3, and A 5 we similarly obtain

$$E_\theta = i\sum_n (W_n J_{n-1} - Z_n J_{n+1})e^{in\theta}. \tag{A 7}$$

The coefficients A_n, W_n, and Z_n are not independent. Substituting Eqs. A 1, A 6, and A 7 into the Maxwell equation $\nabla \cdot \tilde{E} = 0$, which in cylindrical coordinates is

$$\frac{1}{r}\frac{\partial}{\partial r}(rE_r) + \frac{1}{r}\frac{\partial E_\theta}{\partial \theta} + ikE_z = 0,$$

we obtain

$$W_n J'_{n-2} + Z_n J'_{n+1} + \frac{1}{ur}[W_n J_{n-1} + Z_n J_{n+1} - nW_n J_{n-1} + nZ_n J_{n+1}] + \frac{ik}{u} A_n J_n = 0;$$

Using the recurrence relations for the Bessel functions (13) we obtain

$$-W_n J_n + Z_n J_n + \frac{ik}{u} A_n J_n = 0.$$

Since this holds for all values of the argument of the Bessel function this yields

$$Z_n - W_n + \frac{ik}{u} A_n = 0. \quad (A\ 8)$$

The z component of the magnetic field can be written

$$B_z = \sum_n B_n J_n(ur)\, e^{in\theta}. \quad (A\ 9)$$

This is related to the electric fields E_θ and E_r by the Maxwell equation $i\omega/c\, \tilde{B} = \nabla \times \tilde{E}$. In cylindrical coordinates the relevant component for our purpose is

$$\frac{i\omega}{c} B_z = \frac{1}{r}\left(E_\theta - \frac{\partial E_r}{\partial \theta}\right) + \frac{\partial E_\theta}{\partial r}. \quad (A\ 10)$$

Substituting Eqs. A 6, A 7, and A 9 into Eq. A 10 we obtain

$$W_n J'_{n-1} - Z_n J'_{n+1} + \frac{1}{ur}[W_n J_{n-1} - Z_n J_{n+1} - nW_n J_{n-1} - nZ_n J_{n+1}] = \frac{\omega}{cu} B_n J_n.$$

Again using the recurrence relations we obtain

$$-W_n - Z_n = \frac{\omega}{cu} B_n. \quad (A\ 11)$$

Eqs. A 8 and A 11 determine the coefficients E_r E_θ of the electric fields in terms of the coefficients of E_z and B_z. Solving the equations for W_n and Z_n in terms of A_n and B_n and then substituting into the expressions A 6 and A 7 we obtain the expressions 9 and 10 quoted in the main text. The expressions 14 and 15 follow in a similar manner.

APPENDIX II

To reduce Eq. 69 we must integrate Eq. 66 over k. The general method is well illustrated by a particular example. Consider for example, the second term on the right hand side of Eq. 66. This gives an integral

$$I = \int_0^\infty dk \left(\frac{\epsilon_3}{\nu_3^2} - \frac{\epsilon_2}{\nu_2^2}\right) \nu_3^6 K_1^2(\nu_3 R). \quad \text{(A 12)}$$

Introduce new variables

$$p = \frac{c}{\xi\sqrt{\epsilon_3}} \nu_0, \quad \text{(A 13)}$$

and

$$s_2 = \left[p^2 - 1 + \frac{\epsilon_2}{\epsilon_3}\right]^{1/2}. \quad \text{(A 14)}$$

I can now be expressed as

$$I = \left(\frac{\xi\sqrt{\epsilon_3}}{c}\right)^5 (\epsilon_3 - \epsilon_2) \int_1^\infty dp \frac{p^4(p^2-1)^{1/2}}{S_2^2} K_1^2\left(\frac{\xi\sqrt{\epsilon_3}R}{c} p\right). \quad \text{(A 15)}$$

We are interested in the retarded contribution to the free energy, i.e., when $\xi\sqrt{\epsilon_3}R/c \gg 1$. Therefore we can replace the Bessel function by its asymptotic form for large argument (13). This yields

$$I = \left(\frac{\xi\sqrt{\epsilon_3}}{c}\right)^4 \frac{\pi}{2R} (\epsilon_3 - \epsilon_2) \int_1^\infty dp \frac{p^4(p^2-1)^{1/2}}{S_2^2} \exp\left[-(2\xi\sqrt{\epsilon_3}R/c)p\right]. \quad \text{(A 16)}$$

The substitution $p = \cosh u$ now yields

$$I = \left(\frac{\xi\sqrt{\epsilon_3}}{c}\right)^4 \frac{\pi}{2R} (\epsilon_3 - \epsilon_2) \int_0^\infty du \frac{\sinh^2 u \cosh^4 u}{\left(\cosh^2 u + \frac{\epsilon_2}{\epsilon_3} - 1\right)} \cdot \exp\left[-(2\xi\sqrt{\epsilon_3}R/c)\cosh u\right]. \quad \text{(A 17)}$$

In most cases the distance regime is such that retardation is of significance only for high frequencies (i.e., visible, ultraviolet). In this region $\epsilon_2 \sim \epsilon_3 \sim 1$. The denominator can now be simplified and we obtain

$$I = \left(\frac{\xi\sqrt{\epsilon_3}}{c}\right)^4 \frac{\pi}{2R} (\epsilon_3 - \epsilon_2) \int_0^\infty du \sinh^2 u \cosh^2 u \cdot \exp\left[-(2\xi\sqrt{\epsilon_3}R/c)\cosh u\right]. \quad \text{(A 18)}$$

The integral over u can be evaluated exactly after we note that

$$\sinh^2 u \cosh^2 u = \frac{1}{8}[\cosh 4u - 1]. \quad \text{(A 19)}$$

We obtain

$$I = \left(\frac{\xi \sqrt{\epsilon_3}}{c}\right)^4 \frac{\pi}{2R} \frac{(\epsilon_3 - \epsilon_2)}{8} \left[K_4\left(\frac{2\xi \sqrt{\epsilon_3}R}{c}\right) - K_0\left(\frac{2\xi \sqrt{\epsilon_3}R}{c}\right)\right] \quad \text{(A 20)}$$

Again we replace the Bessel functions by their asymptotic form for large argument. The leading terms cancel and it is necessary to go to second order in the expansion which is

$$K\nu(z) \sim \sqrt{\frac{\pi}{2z}}\, e^{-z}\left\{1 + \frac{4\nu^2 - 1}{8z} \cdots\right\}. \quad \text{(A 21)}$$

Substituting this expression into Eq. A 20 we finally obtain

$$I = \left(\frac{\xi \sqrt{\epsilon_3}}{c}\right)^{5/2} \frac{\pi^{3/2}}{2R^{5/2}} \frac{(\epsilon_3 - \epsilon_2)}{8} \frac{63}{64} \cdot \exp\left[-(2\xi \sqrt{\epsilon_3}R/c)\right]. \quad \text{(A 22)}$$

If the frequency regime is such that $\epsilon_2/\epsilon_3 \ll 1$ or $\gg 1$ then different expansions must be used for the denominator in Eq. A 17. The final result, however, does not differ significantly from the one above. The other integrals are done in an identical way.