VAN DER WAALS FORCES BETWEEN CYLINDERS

I. NONRETARDED FORCES BETWEEN THIN ISOTROPIC RODS AND FINITE SIZE CORRECTIONS

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ABSTRACT The free energy of interaction of two long thin dielectric cylinders is evaluated in the nonretarded limit by the method of van Kampen. The result includes all nonadditive many body forces and the effects of an intervening medium. In the limit of dilute systems the result reduces to that obtained by summation of r^{-6} pair potentials.

INTRODUCTION

Recent applications and extensions of the Lifshitz continuum theory of van der Waals forces by Dzyaloshinskii et al. (1) have shed a good deal of new light on the special nature of these forces in condensed media interactions. The various new features which have emerged so far from these applications have been extensively documented elsewhere (see e.g., the work of Parsegian and Ninham [2–4]). Most of this new work has been confined to interactions between planar media, and these interactions do seem to be quite well understood, both qualitatively and quantitatively. By now it appears that the Lifshitz theory provides a quite remarkably diverse theoretical and practical framework. From this framework it is possible, for example, that a theory of the specificity of macromolecular forces may ultimately emerge. Before even beginning to contemplate problems of such obvious complexity, however, it is necessary to develop our intuition concerning van der Waals forces still further. Granted that we understand in some measure the very complicated interplay of effects due to material properties, of ultraviolet and infrared correlations, of microwave correlations and associated entropically driven effects, and of temperature, retardation, and adsorbates, in interactions between *planar* media, it is essential to study the influence of geometry and size on the forces. A start on this problem has been made by several authors (5–9). Some new features which arise as a consequence of spherical geometry and size are already explicit in the work of the latter authors.

In developing this intuition there are clearly two separate aspects. One is the *mathematical* problem of deriving in a usable form, the necessarily complicated formulae which characterize the interactions. The other aspect of the problem is the more difficult and involves the actual application of such formulae to real biological systems. The mathematical problem can be tackled in either of two ways. Either one can seek very general perturbation or variational methods which apply to interacting bodies of arbitrary shape and size, or one can attempt to develop special formulae for simple geometries. In this and several succeeding papers, we adopt the last approach and study the van der Waals forces between two dielectric bodies of cylindrical shape. The present paper deals only with the interaction between parallel thin circular cylinders in the limit that retardation can be ignored. From the work of Parsegian and Ninham (2) one expects that microwave correlations, which are nonretarded, may well dominate the gross features of the interaction so that the problem is not academic. In the following paper we deal with the corresponding generalization which includes retardation.

Various biological systems involve interactions between cylindrical structures. Such structures occur in muscle (10), in viral assembly, in liquid crystals (11), in flagellae, and in the rhabdomeres of insect eyes; linear polyelectrolytes like DNA can be considered as thin cylinders, and so on. The mathematical problem which concerns us reduces essentially to one of determining the coupled surface mode solutions of Maxwell's equations, and the methods we use are identical with those developed elsewhere by other authors (12–14). The solution of the surface mode problem also has some relevance to the study of various optical systems.

FORMULATION

We consider two straight parallel circular cylinders "1" and "2" of radii a and b, and dielectric susceptibilities ϵ_1 and ϵ_2, respectively. The cylinders are immersed in a medium of susceptibility ϵ_3 and have length L. Fig. 1 shows a horizontal cross-section. Suppose that the center-to-center separation is R. The position of an arbitrary point P can be described using two separate sets of cylindrical coordinates, one for each cylinder as indicated in Fig. 1. These have a common z axis parallel to the cylinder axes.

To determine the free energy of interaction between the cylinders, we now follow van Kampen et al. (12) and Ninham et al. (13). In the nonretarded limit ($c \to \infty$)

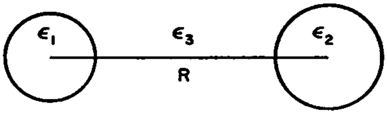

FIGURE 1 The two cylinders are of radius a and b and have dielectric susceptibilities ϵ_1 and ϵ_2, respectively. The center-to-center separation is R. The intervening medium has susceptibility ϵ_3.

the electric potential Φ satisfies Laplace's equation at any point P, i.e.,

$$\nabla^2 \Phi = 0. \tag{1}$$

The general solution has the form

$$\Phi = \phi\, e^{i(kz-\omega t)}, \tag{2}$$

where $k = 2n\pi/L$, $n = 0, \pm 1, \pm 2, \cdots$, and we use periodic boundary conditions for convenience only. Substituting Eq. 2 into Eq. 1 we deduce that ϕ satisfies Helmholtz's equation

$$\nabla^2_{r,\theta}\, \phi - k^2\phi = 0, \tag{3}$$

where $\nabla^2_{r,\theta}$ is the two-dimensional Laplacian in radical polar coordinates. For our system the general solution of Eq. 3 can be written down immediately as

$$\phi = \phi_1 + \phi_3 \qquad r_1 < a, \quad r_2 > b, \tag{4}$$

$$\phi = \phi_2 + \phi_3 \qquad r_1 > a, \quad r_2 > b, \tag{5}$$

$$\phi = \phi_2 + \phi_4 \qquad r_1 > a, \quad r_2 < b, \tag{6}$$

where

$$\phi_1 = \sum_{m=-\infty}^{\infty} A_m \frac{I_m(kr_1)}{I_m(ka)}\, e^{im\theta_1}, \tag{7}$$

$$\phi_2 = \sum_{m=-\infty}^{\infty} A_m \frac{K_m(kr_1)}{K_m(ka)}\, e^{im\theta_1}, \tag{8}$$

$$\phi_3 = \sum_{m=-\infty}^{\infty} C_m \frac{K_m(kr_2)}{K_m(kb)}\, e^{im\theta_2}, \tag{9}$$

$$\phi_4 = \sum_{m=-\infty}^{\infty} C_m \frac{I_m(kr_2)}{I_m(kb)}\, e^{im\theta_2}. \tag{10}$$

The functions I_m, K_m are modified Bessel functions in standard notation, and A_m, C_m are coefficients to be determined. The potentials expressed in the form Eqs. 4–10 are automatically continuous across the surface of the cylinders. It remains to match the normal components of the displacement vector across the cylinder surfaces. This can be done most simply if we note first the addition theorem (15)

$$K_m(kr_2)\, e^{im\theta_2} = \sum_{j=-\infty}^{\infty} K_{m+j}(kR)\, I_j(kr_1)\, e^{ij\theta_1}, \tag{11}$$

together with a similar relation with $r_1 \leftrightarrow r_2$, $\theta_1 \leftrightarrow \theta_2$.

Consider now cylinder 1. From Eqs. 4 and 5 continuity of the normal component of the displacement vector requires that

$$\epsilon_1 \frac{\partial}{\partial r_1}(\phi_1 + \phi_3) = \epsilon_3 \frac{\partial}{\partial r_1}(\phi_2 + \phi_3), \tag{12}$$

or on rearrangement

$$\epsilon_1 \frac{\partial \phi_1}{\partial r_1} - \epsilon_3 \frac{\partial \phi_2}{\partial r_1} = (\epsilon_3 - \epsilon_1)\frac{\partial \phi_3}{\partial r_1}. \tag{13}$$

Here the derivatives are to be evaluated on the surface of cylinder 1, i.e., at $r_1 = a$. From Eqs. 9 and 11 we have

$$\phi_3 = \sum_{m=-\infty}^{\infty} \frac{C_m}{K_m(kb)} \sum_{j=-\infty}^{\infty} K_{m+j}(kR) I_j(kr_1)\, e^{ij\theta_1}. \tag{14}$$

If the potentials given by Eqs. 7, 8, and 14 are substituted into Eq. 13 the derivatives with respect to r_1 can be taken at once. Then equating coefficients of $e^{in\theta_1}$ we obtain a relation between A_n, C_n which is

$$A_n\left\{\epsilon_1 \frac{I_n'(ka)}{I_n(ka)} - \epsilon_3 \frac{K_n'(ka)}{K_n(ka)}\right\} = (\epsilon_3 - \epsilon_1) I_n'(ka) \sum_{m=-\infty}^{\infty} C_m \frac{K_{m+n}(kR)}{K_m(kb)}. \tag{15}$$

This equation can be conveniently expressed in terms of a matrix $\tilde{M}$ as

$$\tilde{A} = \tilde{M}\tilde{C}, \tag{16}$$

where the matrix elements are given by

$$M_{nm} = \frac{(\epsilon_3 - \epsilon_1) I_n'(ka) I_n(ka) K_n(ka) K_{m+n}(kR)}{\{\epsilon_1 I_n'(ka) K_n(ka) - \epsilon_3 I_n(ka) K_n'(ka)\} K_m(kb)}. \tag{17}$$

An equation similar to Eq. 15 where $A \leftrightarrow C$, $\epsilon_1 \leftrightarrow \epsilon_2$, and $a \leftrightarrow b$ follows through the requirement that the normal component of the displacement vector be continuous across cylinder 2. Thus, corresponding to Eqs. 16 and 17 we have

$$\tilde{C} = \tilde{N}\tilde{A}, \tag{18}$$

where

$$N_{nm} = \frac{(\epsilon_3 - \epsilon_2) I_n'(kb) I_n(kb) K_n(kb) K_{m+n}(kR)}{\{\epsilon_2 I_n'(kb) K_n(kb) - \epsilon_3 I_n(kb) K_n'(kb)\} K_m(ka)}. \tag{19}$$

Together Eqs. 16 and 18 provide a condition for consistency and the dispersion relation which determines allowed surface modes follows as

$$\text{Det }(1 - \tilde{\Omega}) = 0; \tilde{\Omega} = \tilde{M}\tilde{N}. \tag{20}$$

Formally, Eq. 20 solves the problem completely. Following Ninham et al. (13) and Richmond and Ninham (14), we sum over all allowed frequencies ω_n and over all values of k, and obtain the free energy of interaction of the cylinders as

$$G(T, a, b, R) = kT \sum_k \sum_n \ln \sinh (\tfrac{1}{2}\hbar\omega_j/kT),$$

$$= \frac{kTL}{\pi} \sum_{n=0}^{\infty}{}' \int_0^{\infty} dk \ln [\text{Det }(1 - \tilde{\Omega})] \tag{21}$$

In Eq. 21 the susceptibilities $\epsilon_j = \epsilon_j(i\xi_n)$ are to be evaluated on the imaginary frequency axis at frequencies $\xi_n = 2\pi nkT/,\hbar\ n = 0, 1, 2, \cdots, \infty$. The prime on the summation symbol means that the term in $n = 0$ is to be taken with a factor $\tfrac{1}{2}$.

DISPERSION RELATION FOR THIN CYLINDERS

While Eq. 20 gives the formal solution to our problem, the evaluation of the determinant is a matter of considerable complexity. We confine explicit analysis in the following to the case of "thin" cylinders $a, b \ll R$. In that case the determinant can be evaluated approximately as follows: returning first to the matrix elements defined by Eqs. 17 and 19 we note first that in the region $kR < 1$, we can expand the Bessel functions in powers of ka, kb, kR to obtain

$$M_{nm} \sim \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right) \frac{(n + m - 1)!}{m!(n - 1)!} \frac{a^n b^m}{R^{m+n}} < 2^{n+m-1} \frac{a^n b^m}{R^{m+n}}, \qquad n, m \geq 1. \tag{22}$$

Hence for $kR < 1$ and $a/R, b/R \ll 1$ the elements M_{nm} (and likewise N_{nm}, Ω_{nm}) are rapidly decreasing functions of n and m. Second we note that since $K_m(kR) \sim e^{-kR}/(kR)^{1/2}$ for $kR \gg 1$ in this region the matrix elements of $\tilde{M}$, $\tilde{N}$, and $\tilde{\Omega}$ decrease rapidly for all m. This suggests that to first approximations we need retain only matrix elements for $n, m = 0, \pm 1$ to leading order. To second approximation only those up to and including $n, m = \pm 2$ are necessary. Further, since the matrix elements are dominated by exponentials for $kR > 1$, only values of $k < 1/R$ are important. Hence the Bessel functions of argument ka and kb can be expanded in powers of ka and kb.

For convenience we introduce the notation

$$\Delta_n(a) = \frac{(\epsilon_3 - \epsilon_1)I_n'(ka)I_n(ka)}{\{\epsilon_1 I_n'(ka)K_n(ka) - \epsilon_3 I_n(ka)K_n'(ka)\}}, \tag{23}$$

$$\Delta_n(b) = \Delta_n(a)\{\epsilon_1 \rightarrow \epsilon_2, a \rightarrow b\}. \tag{24}$$

It follows from Eqs. 17–24 that a general matrix element of $\tilde{\Omega}$ is

$$\Omega_{nm} = \sum_{j=-\infty}^{\infty} \Delta_n(a)\, \Delta_j(b)\, K_{n+j}(kR)\, K_{m+j}(kR). \tag{25}$$

Expanding the Δ's in powers of a/R, b/R and substituting into Eq. 21 it can be shown that off diagonal elements of the determinant give rise to contributions to the free energy which are $O[(ab/R^2)^4]$. These can be ignored to the order of approximation which concerns us. Hence

$$\begin{aligned} \text{Det}\,(1 - \tilde{\Omega}) &= 1 - \sum_{n=-\infty}^{\infty} \Omega_{nm} + O[(ab/R^2)^4], \\ &\simeq 1 - \sum_{n=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \Delta_n(a)\, \Delta_j(b)\, K_{n+j}^2\,(kR). \end{aligned} \tag{26}$$

In the remaining sums only those terms for which $-2 \leq n \leq 2$, $-2 \leq j \leq 2$ need be retained. Terms for which $|\,n\,| = |\,j\,| = 2$ can also be dropped. We then obtain

$$\begin{aligned} \text{Det}\,(1 - \tilde{\Omega}) = 1 &- \Delta_0(a)\Delta_0(b)K_0^2(kR) - 2[\Delta_0(a)\Delta_1(b) + \Delta_1(a)\Delta_0(b)]K_1^2(kR) \\ &- 2\Delta_1(a)\Delta_1(b)[K_0^2(kR) + K_2^2(kR)] \\ &- 2[\Delta_0(a)\Delta_2(b) + \Delta_2(a)\Delta_0(b)]K_2^2(kR) \\ &- 2[\Delta_1(a)\Delta_2(b) + \Delta_2(a)\Delta_1(b)][K_1^2(kR) + K_3^2(kR)]. \end{aligned} \tag{27}$$

Using the limiting form of the Bessel functions for small argument (16) we find after some algebra that

$$\begin{aligned} \Delta_0(ka) &= \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3}\right)\frac{(ka)^2}{2} - \frac{(ka)^4}{4}\left[\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3}\right)\left(\ln ka + \gamma - \ln 2 - \frac{3}{4}\right)\right], \\ \Delta_1(ka) &= \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\frac{(ka)^2}{2} + \frac{(ka)^4}{4} \\ &\quad \cdot\left\{\left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\left(\ln ka - \frac{1}{2}\,[\psi(1) + \psi(2)] + \frac{3}{4} - \ln 2\right) + 1\right\}, \\ \Delta_2(ka) &= \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\frac{(ka)^4}{16}. \end{aligned} \tag{28}$$

Higher powers of k in these expansions lead to terms in the final expressions below which are ignorable to the order of approximation which concerns us. In Eqs. 28 $\psi(2)$ is the logarithmic derivative of the gamma function, and γ is Euler's constant.

We now substitute Eqs. 28 into Eq. 27 and Eq. 27 in turn into the general expression Eq. 21 for the free energy of interaction. One further simplication is possible, as the logarithm of the determinant can be expanded, and only the first term retained to terms of order $[(ab)^2/R]^4$. When these manipulations have been carried out we are left with the sum of a series of integrals. Typical of these is the integral

$$I = \int_0^\infty \Delta_0(a)\Delta_0(b)K_0^2(kR)\,\mathrm{d}k, \tag{29}$$

where from Eq. 28

$$\Delta_0(a)\Delta_0(b) = \left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_2}\right)k^4\frac{a^2b^2}{4} - \left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3}\right)\frac{k^6}{8}a^2b^2$$
$$\cdot\left\{a^2\left[\frac{(\epsilon_3-\epsilon_1)}{\epsilon_3}(\ln ka+\gamma-\ln 2)-\frac{3}{4}\right]\right.$$
$$\left. + b^2[2\rightarrow 1, a\rightarrow b\right\}. \tag{30}$$

This integral can be evaluated using the identities (17)

$$\int_0^\infty k^{s-1}\,K_\mu^2(kR)\,\mathrm{d}k = 2^{s-3}\,R^{-s}\left[\Gamma\left(\frac{1}{2}s\right)\right]^2 B\left(\frac{1}{2}s+\mu, \frac{1}{2}s-\mu\right),$$

where B is a beta function, and

$$\int_0^\infty k^{s-1}\ln kK_\mu^2(kR)\,\mathrm{d}k = \frac{\partial}{\partial s}\int_0^\infty k^{s-1}K_\mu^2(kR)\,\mathrm{d}k. \tag{31}$$

Thus, for example, Eq. 29 becomes

$$I = \left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3}\right)\left\{\frac{a^2b^2}{R^5}\Gamma^2\left(\frac{5}{2}\right)B\left(\frac{5}{2};\frac{5}{2}\right)\right.$$
$$-\frac{2a^4b^2}{R^7}\left[\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\left(\gamma+\ln\frac{a}{2R}\right)-\frac{3}{4}\right]\Gamma^2\left(\frac{7}{2}\right)B\left(\frac{7}{2};\frac{7}{2}\right)$$
$$-(1\rightarrow 2, a\leftrightarrow b)-\frac{2a^2b^2}{R^7}\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\Gamma^2\left(\frac{7}{2}\right)B\left(\frac{7}{2};\frac{7}{2}\right)$$
$$\left.\cdot\left[\ln 2+2\psi\left(\frac{7}{2}\right)-\psi(7)\right]-(1\rightarrow 2, a\leftrightarrow b)\right\}. \tag{32}$$

After evaluating all required integrals, we obtain finally for the free energy of interaction of the cylinders the result

$$G(T,A,B,R) = -\frac{kT}{\pi}\frac{a^2b^2}{R^5}\sum_{n=0}^{\infty}{}' \left\{\frac{4\Gamma^2\left(\frac{5}{2}\right)}{\Gamma(5)}\left[\left(\frac{\epsilon_3-\epsilon_1}{2\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_2}{2\epsilon_3}\right)\Gamma^2\left(\frac{5}{2}\right)\right.\right.$$

$$+\left[\left(\frac{\epsilon_3-\epsilon_2}{2\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3-\epsilon_1}\right)+\left(\frac{\epsilon_3-\epsilon_1}{2\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\right]\Gamma\left(\frac{7}{2}\right)\Gamma\left(\frac{3}{2}\right)$$

$$\left.+\frac{1}{2}\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3+\epsilon_1}\right)\left[\Gamma^2\left(\frac{5}{2}\right)+\Gamma\left(\frac{9}{2}\right)\Gamma\left(\frac{1}{2}\right)\right]\right]$$

$$\left.+\frac{\delta}{R^2}+O\left[\left(\frac{a}{R}\right)^4\ln\frac{a}{R}\right]\right\}. \tag{33}$$

The correction term in δ which determine how rapidly the thin cylinder approximation breaks down as R decreases is somewhat more complicated. Explicitly we have

$$\delta = \frac{4\Gamma^2\left(\frac{7}{2}\right)}{\Gamma(7)}b^2\left\{-\frac{\Delta_0}{2}\Gamma^2\left(\frac{7}{2}\right)\left(-\frac{3}{4}+\left[\frac{\epsilon_3-\epsilon_2}{\epsilon_2}\right]\left[\gamma+2\psi\left(\frac{7}{2}\right)-\psi(7)\right.\right.\right.$$

$$\left.\left.+\ln\frac{b}{R}\right]\right)+\Delta_1\Gamma\left(\frac{9}{2}\right)\Gamma\left(\frac{5}{2}\right)\left[1+\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\left(\frac{3}{4}-\frac{1}{2}[\psi(1)+\psi(2)]\right.\right.$$

$$\left.\left.+\psi\left(\frac{7}{2}\right)-\psi(7)-\frac{1}{2}\left[\psi\left(\frac{9}{2}\right)+\psi\left(\frac{5}{2}\right)\right]+\ln\frac{b}{R}\right)\right]$$

$$-\Delta_1\Gamma\left(\frac{9}{2}\right)\Gamma\left(\frac{5}{2}\right)\left[-\frac{3}{4}+\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\right.$$

$$\left.\cdot\left(\gamma+\psi\left(\frac{7}{2}\right)-\psi(7)-\frac{1}{2}\left[\psi\left(\frac{9}{2}\right)+\psi\left(\frac{5}{2}\right)\right]+\ln\frac{a}{R}\right)\right]$$

$$+\Delta_2\Gamma^2\left(\frac{7}{2}\right)\left[1+\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\left(\frac{3}{4}-\frac{1}{2}\left[\psi(1)+\psi(2)\right]\right.\right.$$

$$\left.\left.+2\psi\left(\frac{7}{2}\right)-\psi(7)+\ln\frac{b}{r}\right)\right]$$

$$+\Delta_2\Gamma\left(\frac{11}{2}\right)\Gamma\left(\frac{3}{2}\right)\left[1+\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\left(\frac{3}{4}-\frac{1}{2}[\psi(1)+\psi(2)]\right.\right.$$

$$\left.\left.+\psi\left(\frac{7}{2}\right)-\psi(7)+\frac{1}{2}\left[\psi\left(\frac{11}{2}\right)+\psi\left(\frac{3}{2}\right)\right]+\ln\frac{b}{R}\right)\right]$$

$$+\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\frac{\Gamma\left(\frac{11}{2}\right)\Gamma\left(\frac{3}{2}\right)}{4}+\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3+\epsilon_1}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\frac{\Gamma\left(\frac{9}{2}\right)\Gamma\left(\frac{5}{2}\right)}{4}$$

$$\left.+\left(\frac{\epsilon_3-\epsilon_1}{\epsilon_3+\epsilon_1}\right)\left(\frac{\epsilon_3-\epsilon_2}{\epsilon_3+\epsilon_2}\right)\frac{\Gamma\left(\frac{13}{2}\right)\Gamma\left(\frac{1}{2}\right)}{4}\right\}+\frac{4\Gamma^2\left(\frac{7}{2}\right)}{\Gamma(7)}a^2\{1\to 2, a\leftrightarrow b\}. \tag{34}$$

In Eq. 34 Δ_0, Δ_1, Δ_2 are defined by

$$\Delta_0 = \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_2}\right),$$

$$\Delta_1 = \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3}\right)\left(\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 + \epsilon_2}\right),$$

$$\Delta_2 = \left(\frac{\epsilon_3 - \epsilon_1}{\epsilon_3 + \epsilon_1}\right)\left(\frac{\epsilon_3 + \epsilon_2}{\epsilon_3 + \epsilon_2}\right). \quad (35)$$

In the general formula, the susceptibilities of the interacting media $\epsilon_j = \epsilon_j(i\xi_n)$ are to be evaluated on the imaginary frequency axis at frequencies $\xi_n = 2\pi nkT/\hbar$. A method by which dielectric data can be fed into Eq. 33 for computation has been developed and applied extensively elsewhere (2–4, 18–22).

LIMITING CASE OF PAIRWISE SUMMATION

As a check on the rather complicated expression, we consider the special limiting case of zero temperature and dilute media interacting across a vacuum ($\epsilon_3 = 1$, $\epsilon_1 - 1 \ll 1$, $\epsilon_2 - 1 \ll 1$). For simplicity we take $\epsilon_2 = \epsilon_1$, and identical radii $a = b$ for the cylinders. In this limit we must, of course, recover the result which follows from pairwise summation of London forces. To reduce our expression to this degenerate case we first note that the sums over n in Eq. 33 become integrals through the transformation

$$kT \sum_{n=0}^{\infty}{}' \rightarrow \frac{\hbar}{2\pi} \int_0^{\infty} d\xi. \quad (36)$$

In the resulting integral we may put $\epsilon_3 = \epsilon_1 = \epsilon_2 = 1$ wherever these occur in a denominator. Further, terms in δ which are of the third order in $(\epsilon_3 - \epsilon_1)$, $(\epsilon_3 - \epsilon_2)$ can be dropped. Such terms are strictly nonadditive and have no counterpart in pairwise summation. Carrying out these reductions we have

$$C(0, a, a, R) \rightarrow -\frac{3^2 a^4}{2^7 R^5} \hbar \int_0^{\infty} d\xi (1 - \epsilon_1)^2 \left[1 + \frac{25}{4} \frac{a^2}{R^2}\right]. \quad (37)$$

For a dilute gas

$$\epsilon_1(\omega) = 1 + 4\pi\rho\, \alpha(\omega), \quad (38)$$

where is the density of gas atoms and $\alpha(\omega)$ is the polarizability of an atom. We take

$$\alpha(\omega) = \frac{\alpha_0}{1 - (\omega/\omega_0)^2}, \quad (39)$$

corresponding to a single resonant absorption frequency at $\omega = \omega_0$, and static polarizability α_0. Then substituting $\omega = i\xi$ in Eq. 39 gives

$$\alpha(i\xi) = \frac{\alpha_0}{1 + (\xi/\omega_0)^2}, \qquad 1 - \epsilon_1 = -4\pi\rho\left[\frac{\alpha_0}{1 + (\xi/\omega_0)^2}\right]. \tag{40}$$

Hence the energy of interaction reduces to

$$G(0, a, a, R) = E(a, R) = -\frac{3^2}{2^7}\frac{a^4}{R^5}\left(1 + \frac{25}{4}\frac{a^2}{R^2}\right)\rho^2 \int_0^\infty d\xi \frac{(4\pi\alpha_0)^2}{[1 + (\xi/\omega_0)^2]^2},$$

$$= -\frac{3^2\pi^3 a^4}{32R^5}\left(1 + \frac{25}{4}\frac{a^2}{R^2} + \cdots\right)\hbar\omega_0\alpha_0^2\rho^2. \tag{41}$$

On the other hand, for two atoms of polarizability α given by Eq. 39 the potential energy of interaction is given by the London potential

$$V(r) = -\frac{3\hbar\omega_0}{4r^6}\alpha_0^2, \tag{42}$$

where r is the distance between atoms. Pairwise summation of these forces over all atoms contained in the cylinders gives

$$E(a, R) = -\iint \frac{dx\, dx'\, dy\, dy'\, dz\, dz'}{[(x - x' + R)^2 + (y - y')^2 + (z - z')^2]^3}\frac{3\hbar\omega_0}{4}\alpha_0^2\rho^2 \cdot \begin{Bmatrix}(x^2 + y^2) < a \\ (x'^2 + y'^2) < a\end{Bmatrix}. \tag{43}$$

The integral is elementary and expansion in powers of $1/R$ gives back Eq. 41.

SUMMARY

We have used the method of van Kampen to evaluate the free energy of interaction in the nonretarded limit between two thin dielectric cylinders. The result includes all nonadditive many body effects and effects due to the intervening medium. As stated above, the expression can be evaluated using measured dielectric data. The validity of the very thin cylinder approximation can be tested by evaluating in like manner the finite size corrections. This theory probably accounts quite well for the attractive forces operating during viral assembly processes. Systems like muscle, however, consist of essentially fat close cylinders (10). This case will be discussed elsewhere. Anisotropy is also likely to be significant in many systems where side chains and local changes in geometry occur. This has been discussed by us elsewhere (23).

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