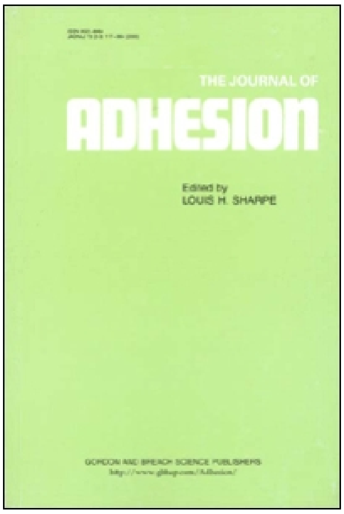

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D. Langbein[a]
[a] Battelle-Institut e.V., Frankfurt/Main, Germany

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*Van Der Waals Attraction Between Macroscopic Bodies

D. Langbein

Battelle-Institut e.V., Frankfurt/Main, Germany

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ABSTRACT

A general dispersion formula is derived, which represents the dispersion energy between two bodies A and B by their macroscopic screened fluctuation fields. These fluctuation fields are calculated exactly in the case of half-spaces and spheres. In the case of half-spaces the Lifshitz dispersion formula is obtained. The dispersion energy between spheres is found to vary as $1/d$ for separations d small compared with the radii and to be proportional to $1/d^6$ for separations d large compared with the radii. The effect of layers adsorbed on the surfaces of the spheres on the dispersion energy is calculated. The dielectric properties of the adsorbed layers predominate over those of the bulk material for separations d smaller than the layer thickness.

INTRODUCTION

IN THIS PAPER we discuss three major subjects:

The first is to conceive a general dispersion formula between macroscopic bodies on the basis of a microscopic approach. The second is to apply this dispersion formula to half-spaces and spheres. The third is to investigate the effect of adsorbed layers on the surfaces of spheres on their dispersion energy.

GENERAL DISPERSION FORMULA

Let us first describe how the general dispersion formula is derived. We consider a macroscopic dielectric body A and assume the Drude model of dispersion, i.e. we represent each molecule in A by a number of harmonic dipole oscillators (Fig. 1). We obtain the electric field of dipole i in A at position j outside of A as follows:

an electric charge at i produces the potential $1/|\mathbf{r}_i - \mathbf{r}_j|$
an electric dipole at i produces the potential $\nabla_i(1/|\mathbf{r}_i - \mathbf{r}_j|)$
an electric dipole at a produces the field

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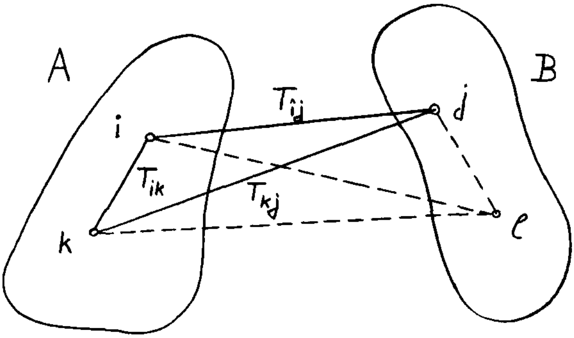

Figure 1. Screening of fluctuation fields.

$$T_{ij} = -\nabla_i \nabla_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

Now, if dipole i is embedded in a dielectric medium A, the field T_{ij} of i at j will be screened by the remaining dipoles $k, m, \ldots$ of A. This screened field T_{ij}^{scr} consists of the direct field T_{ij}, the first-order polarization field $T_{ik}\alpha_k T_{kj}$ of all remaining dipoles k in A, the second-order polarization field $T_{ik}\alpha_k T_{km}\alpha_m T_{mj}$ of all the remaining dipoles k, m in A, and so on.

$$T_{ij}^{scr} = T_{ij} + \sum_{k\epsilon A} T_{ik}\alpha_k T_{kj} + \sum_{k,m\epsilon A} T_{ik}\alpha_k T_{km}\alpha_m T_{mj} + \ldots \tag{2}$$

We are interested in the dispersion energy between two macroscopic bodies A and B. Thus, we consider j to be the position of a dipole in B and calculate also the screened field of dipole j at position i outside of B

$$T_{ji}^{scr} = T_{ji} + \sum_{l\epsilon B} T_{jl}\alpha_l T_{li} + \sum_{l,n\epsilon B} T_{jl}\alpha_l T_{ln}\alpha_n T_{ni} + \ldots \tag{3}$$

We understand that screening is due to that body at which the field originates.

If we calculate the dispersion energy between bodies A and B from the difference between the zero-point energy of the perturbed and that of the unperturbed dipole modes, we obtain [1]

$$\Delta E_{AB} = -\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty} d\omega \left\{ \sum_{i\epsilon A}\sum_{j\epsilon B} \alpha_i T_{ij}^{scr}\alpha_j T_{ji}^{scr} \right. \\ \left. + \frac{1}{2}\sum_{i,k\epsilon A}\sum_{j,l\epsilon B} \alpha_i T_{ij}^{scr}\alpha_j T_{jk}^{scr}\alpha_k T_{kl}^{scr}\alpha_l T_{li}^{scr} + \ldots \right\} \tag{4}$$

We interpret (4) as follows:

Molecule i in A produces spontaneous field fluctuations T_{ij}^{scr}. The intensity of these fluctuations is given by the imaginary part $\alpha_i''(\omega)$ of the polarizability of molecule i. The field T_{ij}^{scr} then polarizes molecule j in B according to the real part $\alpha_j'(\omega)$ of the polarizability of molecule j. The induced field T_{ji}^{scr} lowers the energy of the initial fluctuation of molecule i. Moreover, molecule j polarizes the rest of molecules k in A according to $T_{jk}^{scr}\ \alpha_k'(\omega)$, molecule k polarizes molecule l, molecule l polarizes molecule i, and this lowers the energy of the initial fluctuation, too.

The resulting equation seems non-symmetric with respect to the acting molecule i and the reacting molecules j, k, l, . . . However, the symmetry between molecules i, j, k, l, . . . can be restored by shifting the contour of integration to the imaginary frequency axis, which leaves us with the complex arguments $\alpha_i(i\omega)$, $\alpha_j(i\omega)$, . . . in (4).

We emphasize that only the macroscopic screened fields T_{ij}^{scr} enter the final expression for the dispersion energy. This enables us to calculate ΔE_{AB} from strictly macroscopic considerations.

HALF-SPACES AND SPHERES

The second subject of our program is the application of the macroscopic dispersion formula (4) to half-spaces and spheres.

Let us begin with half-spaces. The direct potential of a point charge i outside a half-space A at position j is $1/|\mathbf{r}_i - \mathbf{r}_j|$. The resulting polarization potential of half-space A is $-\ [($[illegible]$ - \epsilon_3)/(\epsilon_1 + \epsilon_3)]/|\mathbf{r}_i' - \mathbf{r}_j|$ where $\mathbf{r}_i'$ is the image point of i with respect to the surface of A and ϵ_1, ϵ_3 are the dielectric constants of half-space and exterior, respectively. A second half-space B with dielectric constant ϵ_2, which faces A at distance d, in like manner yields the polarization potential $-\ [(\epsilon_2 - \epsilon_3)/(\epsilon_2 + \epsilon_3)]/|\mathbf{r}_i'' - \mathbf{r}_j|$. Thus, the first term in the general dispersion formula (4) contains the factor

$$\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3}\,\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \tag{5}$$

The second term in (4) contains the square of factor (5), and so on. Since each reflection of the image charges at the surface of the opposite half-space increases their distance by twice the separation d, we wind up with

$$\frac{\Delta E_{AB}}{\text{surface area}} = -\frac{\hbar}{16\pi^2 d^2}\int_{-\infty}^{+\infty} d\omega \sum_{\nu=1}^{\infty} \frac{1}{\nu^3}\left(\frac{\epsilon_1(i\omega) - \epsilon_3(i\omega)}{\epsilon_1(i\omega) + \epsilon_3(i\omega)}\,\frac{\epsilon_2(i\omega) - \epsilon_3(i\omega)}{\epsilon_2(i\omega) + \epsilon_3(i\omega)}\right)^{\nu} \tag{6}$$

This is the exact Lifshitz formula for the case of small separations without retardation [2].

Let us now turn to the dispersion energy between two spheres A and B

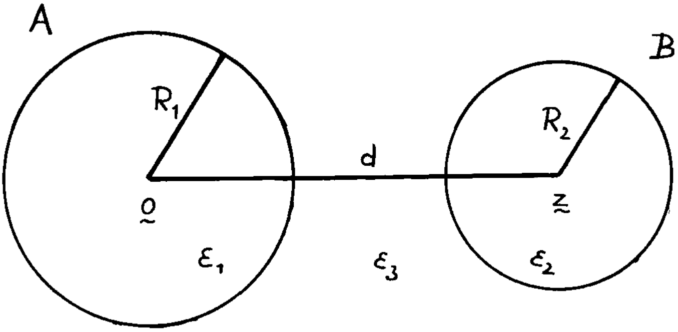

Figure 2. Attracting spheres.

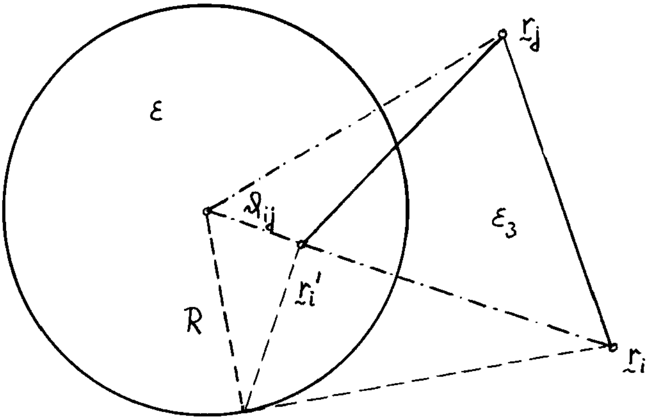

Figure 3. Polarization potential.

with radii R_1, R_2 and dielectric constants ϵ_1, ϵ_2, and let the separation of the centers be $z = d + R_1 + R_2$ (Fig. 2).

We describe the polarization field of half-spaces in terms of image charges. The polarization field of spheres is conveniently expanded in terms of spherical harmonics. We illustrate this by the polarization potential V_{pol} of a point charge at $\mathbf{r}_i$ outside a sphere with radius R and dielectric constant ϵ (Fig. 3), which reads

$$V_{pol} = -\sum_{n=0}^{\infty} \frac{n(\epsilon - \epsilon_3)}{n\epsilon + (n+1)\epsilon_3} \frac{R^{2n+1}}{(r_i r_j)^{n+1}} P_n(\cos \vartheta_{ij}) \tag{7}$$

We note that each polarization of the field by a sphere requires an expansion in terms of spherical harmonics and that the contribution of n^{th}-order spherical harmonics is proportional to the characteristic dielectric quotient

$$\eta_i(n) = \frac{n(\epsilon_i - \epsilon_3)}{n\epsilon_i + (n+1)\,\epsilon_3}\,;\; i = 1, 2 \tag{8}$$

Thus, the first order term of the dispersion energy between spheres A and B results to be [3]

$$\Delta E_{AB} = -\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty} d\omega \sum_{m=1}^{\infty} \eta_1(m)\left(\frac{R_1}{z}\right)^{2m+1} \sum_{n=1}^{\infty} \eta_2(n)\left(\frac{R_2}{z}\right)^{2n+1} \binom{2m+2n}{2n} \tag{9}$$

Convergence of (9) is guaranteed by the fact that the reduced radii R_i/z and the dielectric quotients $\eta_i(n)$ are generally smaller than one. We find an upper and a lower limit for ΔE_{AB}, if we approximate $\eta_i(n)$ according to

$$\frac{2n}{2n+1}\,\frac{\epsilon_i - \epsilon_3}{\epsilon_i + \epsilon_3} \leq \frac{n(\epsilon_i - \epsilon_3)}{n\epsilon_i + (n+1)\,\epsilon_3} \leq \frac{\epsilon_i - \epsilon_3}{\epsilon_i + \epsilon_3} \tag{10}$$

Proportionality of the two limits to $(\epsilon_i - \epsilon_3)/(\epsilon_i + \epsilon_3)$ implies that the corresponding limits for ΔE_{AB} also split up into a frequency and a geometric factor. We obtain the upper limit

$$|\Delta E_{AB}| \leq \frac{\hbar\bar{\omega}}{2\pi} R_1 R_2 \left\{ \frac{1}{2}\left(\frac{1}{z^2 - (R_1+R_2)^2} + \frac{1}{z^2 - (R_1-R_2)^2}\right) - \frac{1}{z^2 - R_1^2} - \frac{1}{z^2 - R_2^2} + \frac{1}{z^2} \right\} = -\Delta E_L \tag{11}$$

and the lower limit

$$|\Delta E_{AB}| \geq \frac{\hbar\bar{\omega}}{2\pi} \left\{ \frac{R_1 R_2}{2}\left(\frac{1}{z^2 - (R_1+R_2)^2} + \frac{1}{z^2 - (R_1-R_2)^2}\right) + \frac{1}{4}\log\frac{z^2 - (R_1+R_2)^2}{z^2 - (R_1-R_2)^2} \right\} = -\Delta E_H \tag{12}$$

where

$$\bar{\omega} = \int_0^{\infty} d\omega\, \frac{\epsilon_1(i\omega) - \epsilon_3(i\omega)}{\epsilon_1(i\omega) + \epsilon_3(i\omega)}\,\frac{\epsilon_2(i\omega) - \epsilon_3(i\omega)}{\epsilon_2(i\omega) + \epsilon_3(i\omega)} \tag{13}$$

The lower limit (12) is essentially the result obtained by Hamaker without considering the screening of the fluctuation field. We find the Hamaker-interaction constant to equal $\hbar\bar{\omega}/2\pi$, as Krupp [4] concluded from analogies among the attraction between two half-spaces and between sphere and half-space.

While the lower limit (12) is obtained without any screening, the upper limit (11) corresponds to maximum screening by half-spaces. This is best

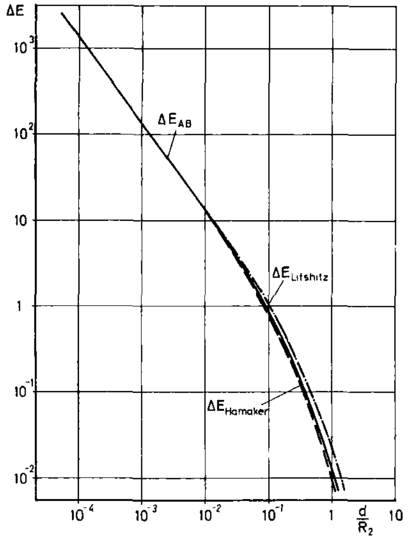

Figure 4. Dispersion energy versus separation.

demonstrated by the example of the polarization potential (7). If we introduce the upper limit (10) we obtain

$$V_{pol} \leqq -\frac{\epsilon-\epsilon_3}{\epsilon+\epsilon_3}\frac{R}{r_i}\frac{1}{|\mathbf{r}_i'-\mathbf{r}_j|} \qquad (14)$$

where $\mathbf{r}_i'$ is the image point of $\mathbf{r}_i$ with respect to the sphere. We again obtain the principle of image charges and the dielectric quotient $(\epsilon-\epsilon_3)/(\epsilon+\epsilon_3)$ characteristic of half-spaces. The additional factor $R/r_i = (R-r_i')/(r_i-R)$ offsets the generally smaller distance between $\mathbf{r}_i$ and $\mathbf{r}_i'$ in the case of spheres (Fig. 3).

Fig. 4 shows the dispersion energy ΔE_{AB} together with its upper and lower limits ΔE_L and ΔE_H. We assumed $R_1 = R_2$ and $\epsilon_1(i\omega) = \epsilon_2(i\omega) = 2$ for ω smaller than an appropriate cut-off frequency ω_0. The unit of the separation is the reduced unit d/R_2. The unit for the dispersion energy ΔE_{AB} is arbitrary and, in this numerical example, depends primarily on the extension of the ω-region, where $\epsilon_1 = \epsilon_2 = 2$ is assumed. Fig. 4 shows very close agreement of the dispersion energy and its upper and lower limits for small separations d, so that the modified Lifshitz formula [3]

$$\Delta E_{AB} \simeq -\frac{\hbar}{8\pi}\int_0^\infty d\omega \sum_{\nu=1}^{\infty}\frac{1}{\nu^3}\left(\frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3}\frac{\epsilon_2-\epsilon_3}{\epsilon_2+\epsilon_3}\right)^{\nu}\frac{R_1R_2}{d(R_1+R_2)} \qquad (15)$$

can be used. This region of separations is characteristic of adhesion measurements involving adhesion of spheres with a diameter of a few 10^{-4} cm at separations of a few 10^{-8} cm from a half-space. In Fig. 4 the values of the exact dispersion energy have been computed by summing the first 120 terms in m and n in (9) exactly and approximating the remaining terms according to (10).

With regard to the dependence of ΔE_{AB} on the dielectric constants ϵ_1, ϵ_2 we note that the lower limit (10) is exact for ϵ_i close to one, whereas for ϵ_i close to infinity the upper limit (10) yields the correct result. The same is also true of the dispersion energy ΔE_{AB}, i.e. with ϵ_i approaching one it approaches the lower limit ΔE_H and with ϵ_i approaching infinity it approaches

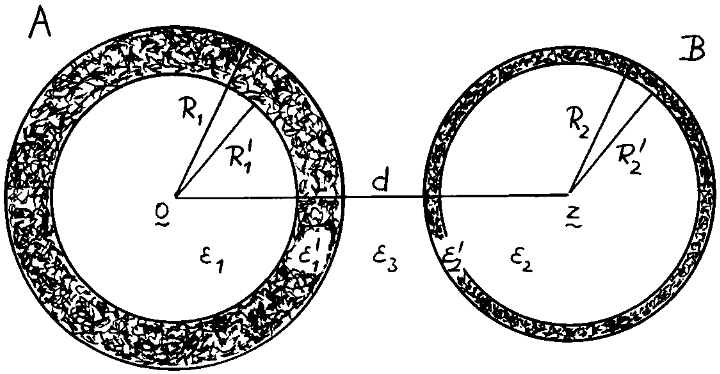

Figure 5. Spheres covered with adsorbates.

the upper limit ΔE_L. By keeping first order correction terms to (10) we obtain the relation

$$\Delta E_{AB} \simeq \frac{1}{\bar{\omega}} \int_0^\infty d\omega \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \left\{ \left(\frac{\epsilon_1}{\epsilon_1 + \epsilon_3} + \frac{\epsilon_2}{\epsilon_2 + \epsilon_3} \right) \Delta E_H + \frac{1}{2} \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} + \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) \Delta E_L \right\} \quad (16)$$

which turns out to be a sufficient approximation for all practical purposes.

ADSORBED LAYERS

Our third subject is the effect of layers adsorbed on the surface of spheres on their dispersion energy (Fig. 5).

A first hint on this influence is obtained by comparing the Lifshitz formula (6) for half-spaces with our result for spheres: The dispersion energy between a half-space and a sphere of radius R equals that between a half-space and a cylinder of surface area $2\pi dR$, if we ignore the different effectiveness of screening in these two cases. $2\pi dR$ is the area of the section of the sphere at twice its distance d from the half-space, which is the position of the first layer of image charges in the system half-space plus cylinder.

This coincidence suggests that the dispersion energy between a half-space and an inhomogeneous sphere is determined primarily by the composition of the sphere in its cross-section at distance $2d$ from the half-space. The dispersion energy between a half-space and a sphere of dielectric constant ϵ, which is covered with an adsorbed layer of dielectric constant ϵ', should be determined by ϵ' for separations d smaller than the layer thickness and by ϵ for separations d larger than the layer thickness.

This suggestion is confirmed by quantitative investigations on the effect of adsorbed layers. If we calculate the polarization potential of a point charge at position $\mathbf{r}_i$ outside a sphere of radius R and dielectric constants ϵ for $r < R'$ and ϵ' for $R' < r < R$, we obtain (7), with $\eta(n)$ replaced by [3]

$$\eta^{ad}(n) = \frac{\dfrac{n(\epsilon' - \epsilon_3)}{n\epsilon' + (n+1)\epsilon_3} + \left(\dfrac{R'}{R}\right)^{2n+1} \dfrac{n(\epsilon - \epsilon')}{n\epsilon + (n+1)\epsilon'} \dfrac{(n+1)\,\epsilon' + n\epsilon_3}{n\epsilon' + (n+1)\epsilon_3}}{1 + \left(\dfrac{R'}{R}\right)^{2n+1} \dfrac{n(\epsilon - \epsilon')}{n\epsilon + (n+1)\epsilon'} \dfrac{(n+1)(\epsilon' - \epsilon_3)}{n\epsilon' + (n+1)\epsilon_3}} \tag{17}$$

The substitution of $\eta_i^{ad}(n)$ for $\eta_i(n)$ again is the only change of the dispersion energy formula between spheres in the presence of adsorbed layers (Fig. 5). If the thickness $R_i - R_i'$ of such an adsorbed layer is small compared with the corresponding radius R_i, we find $\eta_i^{ad}(n)$ to yield an exponential transition from $n(\epsilon_i - \epsilon_3)/[n\epsilon_i + (n+1)\,\epsilon_3]$ for small values of n to $n(\epsilon_i' - \epsilon_3)/[n\epsilon_i' + (n+1)\,\epsilon_3]$ for large values of n. It is a question of the number of terms in m, n needed for convergence of (9), whether the bulk material or the adsorbed layer make the main contribution to the dispersion energy. Since this number of terms is roughly given by the ratio of the radius R_i to the separation d, we find the dispersion energy to be determined by the adsorbed layer if $(R_i'/R_i)^{R_i/d} \lesssim 1$, and by the bulk material if $(R_i'/R_i)^{R_i/d} << 1$.

The effect of an adsorbed layer dominates over that of the bulk material for separations d smaller than the layer thickness, whereas for separations d larger than the layer thickness the bulk material is predominant.

Fig. 6 shows the effect of a layer of varying thickness $R_1 - R_1'$ adsorbed on the surface of sphere A. We plotted the dispersion energy $\Delta E_{AB}(ad)$ of a sphere covered with an adsorbate relative to that of a sphere having a clean surface and identical radius versus the separation d. The parameter of the different curves is the ratio between the inner radius R_1' and the outer radius R_1. The dielectric constant $\epsilon_1'(i\omega)$ of the adsorbed layer is assumed larger than that of the bulk material, $\epsilon_1'(i\omega) = 10$, $\epsilon_1(i\omega) = 2$. From Fig. 6 it is

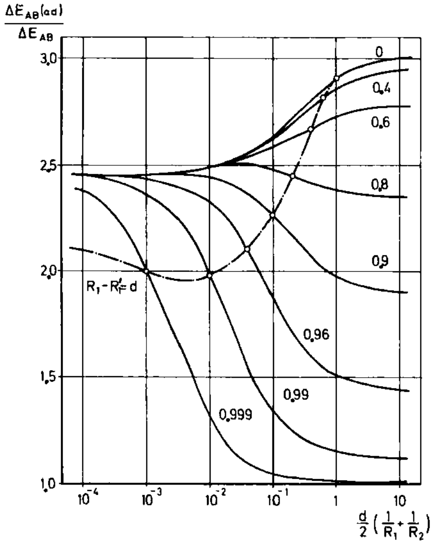

Figure 6. Effect of adsorbed layers.

obvious that it is the adsorbed layer which is effective if the separation d is smaller than the layer thickness. In this region we can expand $\eta_i^{ad}(n)$ in a power series in R_i'/R_i. We obtain approximately

$$\Delta E_{AB} \simeq -\frac{\hbar}{8\pi}\left\{ \overline{\omega}' \frac{R_1 R_2}{d(R_1+R_2)} + \overline{\omega}'' \frac{R_1' R_2}{(d+R_1-R_1')(R_1'+R_2)} \right\} \tag{18}$$

where

$$\overline{\omega}' = \int_0^\infty d\omega \frac{\epsilon_1' - \epsilon_3}{\epsilon_1' + \epsilon_3} \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \tag{19}$$

$$\overline{\omega}'' = \int_0^\infty d\omega \frac{4\,\epsilon_1'\,\epsilon_3}{(\epsilon_1' + \epsilon_3)^2} \frac{\epsilon_1 - \epsilon_1'}{\epsilon_1 + \epsilon_1'} \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \tag{20}$$

The first term in (18) is the dispersion energy between spheres with radii R_1, R_2 and dielectric constants $\epsilon_1'(i\omega)$, $\epsilon_2(i\omega)$. It yields the limit of $\Delta E_{AB}(ad)$ on the left-hand side of Fig. 6.

The second term in (18) is the dispersion energy between spheres with radii R_1', R_2 and dielectric constants $\epsilon_1(i\omega)$, $\epsilon_2(i\omega)$, if sphere A is embedded in a medium with dielectric constant $\epsilon_1'(i\omega)$ and sphere B is embedded in a medium with dielectric constant $\epsilon_3(i\omega)$. The adsorbed layer does not only act as a spacer, but causes an additional screening of the reaction fields.

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