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THE LONDON—VAN DER WAALS ATTRACTION BETWEEN SPHERICAL PARTICLES

by H. C. HAMAKER

Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken Eindhoven-Holland

Summary

Frequently we experience the existance of adhesive forces between small particles. It seems natural to ascribe this adhesion for a large part to London-v. d. Waals forces. To obtain general information concerning their order of magnitude the London-v. d. Waals interaction between two spherical particles is computed as a function of the diameters and the distance separating them. A table is calculated which enables numerical application of the formulae derived. Besides approximations are added, which may be used when the distance between the particles is small. In a separate section it is investigated how the results must be modified, when both particles are immersed in a liquid. Here we are led to the important conclusion that even in that case London-v. d. Waals forces generally cause an attraction.

§ 1. *Introduction.* Frequently we experience the existence of adhesive forces between small particles of any substance or between a particle and a surface. Of this the general occurrence of flocculation in colloidal systems is one of the most striking examples.

It seems natural, to date, to attribute this adhesion mainly to London-v. d. Waals forces and it may be of interest to possess formulae from which the magnitude and range of these forces can be estimated. It is the purpose of this paper to provide some data which may be used for such computations. To simplify the calculations we will consider spherical particles only; in practical problems the particles will mostly be of irregular shape; in such cases the formulae derived below must be applied with caution, a question that will be discussed more in detail in a subsequent paper [1]).

The energy of interaction between two particles containing q atoms per cm^3 is given by:

$$E = -\int_{V_1} dv_1 \int_{V_2} dv_2 \frac{q^2\lambda}{r^6} \qquad (1)$$

where dv_1, dv_2, V_1 and V_2 designate volume elements and total volumes of the two particles respectively, r denotes the distance between dv_1 and dv_2 and λ is the L o n d o n-v d. W a a l s constant.

For spherical particles integral (1) has already been calculated by B r a d l e y [2]). Since he was interested only in approximations valid for small distances he left his complete formulae in an unreduced form unsuited for numerical computations. Besides, one of B r a d l e y's formulae [3]) is not symmetric in r_1 and r_2, the radii of the two particles, and cannot be correct for that reason. I therefore preferred to recalculate integral (1) from the beginning.

In § 2 this integral will be reduced to a form suited for direct integration and will then be integrated. The reader not interested in this purely mathematical question may pass over to § 3, where the resulting formulae have been compiled together with approximations valid for small distances and with a numerical table. In § 4 it will be investigated, how the results must be modified, when the particles are embedded in a fluid. A discussion of experimental data on the basis of these calculations will be given in a separate paper. [1])

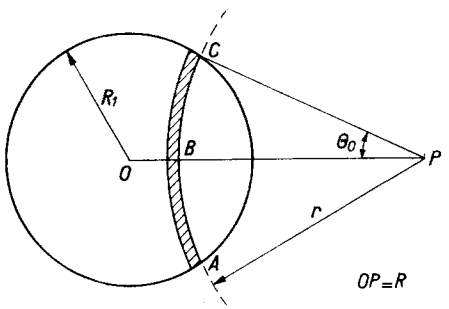

Fig. 1.

§ 2. *Integrations.* Consider (fig. 1) a sphere of radius R_1 and centre O and a point P outside at a distance $OP = R$. The sphere around O will cut out from a second sphere of radius r around P a surface ABC, which is found to be:

$$\text{Surface } (ABC) = \int_0^{2\pi} d\varphi \int_0^{\theta_0} d\theta \, r^2 \sin\theta \tag{2}$$

θ_0 being given by:

$$R_1^2 = R^2 + r^2 - 2rR\cos\theta_0 \tag{3}$$

The integration yields:

$$\text{Surface } (ABC) = \pi \frac{r}{R} \{R_1^2 - (R - r)^2\} \tag{4}$$

and the volume element indicated by the hatched part in fig. 1 is obtained by multiplying this with dr.

The potential energy of an atom at P may now at once be written down as

$$E_P = -\int_{R-R_1}^{R+R_1} \frac{\lambda q}{r^6} \pi \frac{r}{R} \{R_1^2 - (R-r)^2\}\, dr \qquad (5)$$

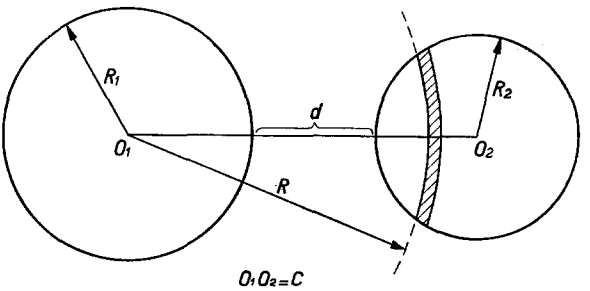

Fig. 2.

With respect to a second sphere of radius R_2, the centres being a distance C apart, the same method may be applied and we obtain for the total energy of interaction (compare fig. 2):

$$E = \int_{C-R_2}^{C+R_2} E_p\, q\, \pi \frac{R}{C} \{R_2^2 - (C-R)^2\}\, dR =$$

$$= \frac{-\pi^2 q^2 \lambda}{C} \int_{C-R_2}^{C+R_2} \{R_2^2 - (C-R)^2\}\, dR \int_{R-R_1}^{R+R_1} \frac{\{R_1^2 - (R-r)^2\}\, dr}{r^5}. \qquad (6)$$

Carrying out the second integration we get:

$$E = \frac{-\pi^2 q^2 \lambda}{C} \int_{C-R_2}^{C+R_2} \{R_2^2 - (C-R)^2\}\, dR \cdot \frac{1}{12} \left\{ \frac{2R_1}{(R+R_1)^3} + \frac{2R_1}{(R-R_1)^3} + \right.$$

$$\left. + \frac{1}{(R+R_1)^2} - \frac{1}{(R-R_1)^2} \right\} \qquad (7)$$

which finally yields:

$$E = -\pi^2 q^2 \lambda \frac{1}{6} \left\{ \frac{2R_1R_2}{C^2 - (R_1+R_2)^2} + \right.$$

$$\left. + \frac{2R_1R_2}{C^2 - (R_1-R_2)^2} + ln \frac{C^2 - (R_1+R_2)^2}{C^2 - (R_1-R_2)^2} \right\}. \qquad (8)$$

This formula expresses the energy E as a function of the radii R_1 and R_2 and of the distance C between the centra. The equation simplifies upon the introduction of another set of variables.

If we take (fig. 2)

$$C = R_1 + R_2 + d \tag{9}$$

d measures the shortest distance between the two particles. Moreover we introduce:

$$x = \frac{d}{2R_1} = \frac{d}{D_1} \qquad y = \frac{D_2}{D_1} = \frac{R_2}{R_1}. \tag{10}$$

Here x gives the ratio of the shortest distance d to the diameter of sphere 1, or in other words, the distance d when D_1 is taken as unity of distance. Likewise y presents the diameter D_2 of sphere 2 expressed in D_1.

Introducing the new variables we obtain:

$$E = -A\frac{1}{12}\left\{\frac{y}{x^2+xy+x} + \frac{y}{x^2+xy+x+y} + 2ln\frac{x^2+xy+x}{x^2+xy+x+y}\right\} \tag{11}$$

where $A = \pi^2 q^2 \lambda$.

This equation will be used in § 3 for numerical computations. We see that E is a function of x and y only; the physical importance of this will be explained later.

§ 3. *Formulae and numerical data.* In § 2 the following result has been reached: The mutual energy of two spheres of diameters D_1 and D_2, a distance d apart and containing q atoms per cm^3 which interact with an energy λ/r^6 is:

$$E = -AE_y(x) = -A\frac{1}{12}\left\{\frac{y}{x^2+xy+x} + \right.$$
$$\left. + \frac{y}{x^2+xy+x+y} + 2\,ln\frac{x^2+xy+x}{x^2+xy+x+y}\right\}. \tag{13}$$

where

$$A = \pi^2 q^2 \lambda \qquad x = \frac{d}{D_1} \qquad y = \frac{D_2}{D_1}. \tag{13a}$$

When $x \ll 1$ (13) is approximated by

$$E = -A\frac{1}{12}\frac{y}{x(y+1)}. \tag{13b}$$ [4])

In the following we will suppose D_1 to measure the diameter of the

smallest of the two spheres; this assumption simplifies the discussion without impairing the generality of the conclusions. x and y now measure the distance and the diameter of the largest sphere in terms of the diameter of the smallest sphere; y will vary between 1 and ∞.

The constant A will be different from case to case, so that we cannot fix one single value. Within what limits A is likely to lie will be discussed in § 4.

Once A is known, a numerical table, representing the function $E_y(x)$ for different values of y and x will furnish all data needed for practical applications.

For two spheres of equal size we have $y = 1$ and

$$E_1(x) = \frac{1}{12}\left\{\frac{1}{x^2+2x} + \frac{1}{x^2+2x+1} + 2\,ln\,\frac{x^2+2x}{x^2+2x+1}\right\} \tag{14}$$

when $x \ll 1$

$$E_1(x) = \frac{1}{24x} \text{ approximately.} \tag{14a}$$

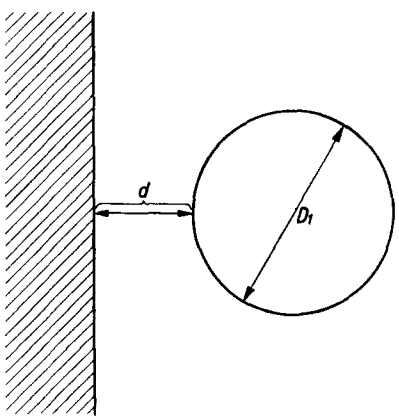

Fig. 3.

Likewise $y = \infty$ represents the case of a sphere and an infinite mass bounded by a flat surface (fig. 3). We have:

$$E_\infty(x) = \frac{1}{12}\left\{\frac{1}{x} + \frac{1}{x+1} + 2\,ln\,\frac{x}{x+1}\right\} \tag{15}$$

and

$$E_\infty(x) = \frac{1}{12x} \text{ when } x \ll 1. \tag{15a}$$

Values of E_1 and E_∞ together with a few intermediate cases have been compiled in table I. As we should expect the values of E_2, E_5 and E_{10} lie between those of E_1 and E_∞. In most practical discussions we may often content ourselves by considering only the latter two, being the extremes.

Sometimes we have to consider forces instead of energies. These are derived from the above formulae by differentiation with respect to d. Since we have

$$\frac{\partial}{\partial d} = \frac{\partial x}{\partial d}\frac{\partial}{\partial x} = \frac{1}{D_1}\frac{\partial}{\partial x}$$

we get from (13)

$$F = \frac{\partial E}{\partial d} = -\frac{A}{D_1}\frac{\partial E_y(x)}{\partial x} = -\frac{A}{D_1}F_y(x) \tag{16}$$

$F_y(x)$ depending on x and y only.

For two equal spheres ($y = 1$) we obtain by differentiation of (14):

$$F_1(x) = \frac{1}{6}\left\{\frac{2(x+1)}{x^2+2x} - \frac{x+1}{(x^2+2x)^2} - \frac{2}{x+1} - \frac{1}{(x+1)^3}\right\} \tag{17}$$

and approximately when $x \ll 1$:

$$F_1(x) = -\frac{1}{24}\frac{1}{x^2}. \tag{17a}$$

Likewise when $y = \infty$ (sphere and flat surface):

$$F_\infty(x) = \frac{1}{12}\left\{\frac{2}{x} - \frac{1}{x^2} - \frac{2}{x+1} - \frac{1}{(x+1)^2}\right\} \tag{18}$$

and when $x \ll 1$

$$F_\infty(x) = -\frac{1}{12}\frac{1}{x^2}. \tag{18a}$$

Numerical values of the functions $F_1(x)$ and $F_\infty(x)$ have been incorporated in table I column 7 and 8.

It will be observed that, given a value of A, the energy E (formula 13) depends on the ratios $x = d/D_1$ and $y = D_2/D_1$ only. If we increase d, D_1 and D_2 in the same ratio, the energy remains unaltered This, however, does no longer hold for the forces; here D_1 enters explicity in the formulae as is seen from (16).

In some experiments the adhesion is studied between two polished surfaces and we will here add the formulae relating to this case. The

London-v. d. Waals potential of a single atom at a distance r from a flat surface is known to be [5]:

$$E_r = -\frac{q\pi\lambda}{6}\frac{1}{r^3}. \tag{19}$$

From this the energy per cm^2 of two flat surfaces a distance d apart is easily derived to be:

$$E = -\int_d^\infty \frac{\pi q\lambda}{6}\frac{1}{r^3}\,q\,dr = -\frac{\pi q^2\lambda}{12d^2} = -\frac{A}{12\pi}\frac{1}{d^2}. \tag{20}$$

The force per cm^2 found by differentiation is:

$$F = \frac{A}{6\pi}\frac{1}{d^3}. \tag{21}$$ [6]

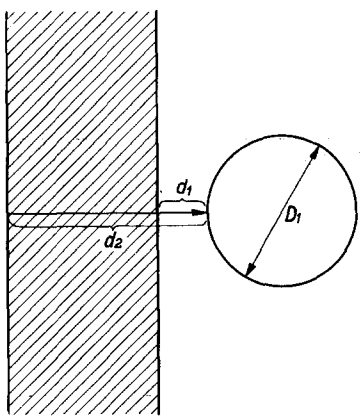

Fig. 4.

Strictly equations 15, 18, 20 and 21 relate to infinite masses bounded by a flat surface. In practice, however, they may also be applied to plates of finite thickness. For instance in the case depicted in fig. 4, the correct value of the energy is:

$$E = -A\,\{E_\infty(x_1) - E_\infty(x_2)\} \tag{22}$$

where $x_1 = d_1/D$ and $x_2 = d_2/D$. But if the sphere is close enough to the surface we have $x_2 \gg x_1$ and consequently $E_\infty(x_2) \ll E_\infty(x_1)$, since $E_\infty(x)$ is a function which rapidly decreases with increasing x. If the sphere is further away, this reasoning does not hold, but then $E_\infty(x_1)$ and $E_\infty(x_2)$ become unmeasurably small that so the case is not of any practical interest.

In the following table the result of numerical calculations based on the formulae given above have been compiled. For values of x smaller than those given in table I the approximate formulae may be used to within a few percents.

TABLE I

	$E_1(x)$	$E_2(x)$	$E_5(x)$	$E_{10}(x)$	$E_\infty(x)$	$-F_1(x)$	$-F_\infty(x)$
$x =$							
0.001	4.07×10^{1}	5.46×10^{1}	6.84×10^{1}	7.47×10^{1}	8.23×10^{1}	4.15×10^{4}	8.62×10^{4}
0.002	2.00×10^{1}	2.69×10^{1}	3.38×10^{1}	3.69×10^{1}	4.07×10^{1}	1.03×10^{4}	2.08×10^{4}
0.005	7.63	1.04×10^{1}	1.31×10^{1}	1.45×10^{1}	1.59×10^{1}	1.63×10^{3}	3.30×10^{3}
0.01	3.58	4.92	6.28	6.90	7.65	4.00×10^{2}	8.17×10^{2}
0.02	1.60	2.25	2.92	3.24	3.59	9.62×10^{1}	2.00×10^{2}
0.05	4.91×10^{-1}	7.46×10^{-1}	9.62×10^{-1}	1.10	1.24	1.37×10^{1}	3.03×10^{1}
0.1	1.74×10^{-1}	2.75×10^{-1}	3.88×10^{-1}	4.42×10^{-1}	5.09×10^{-1}	2.83	6.88
0.2	4.97×10^{-2}	8.74×10^{-2}	1.34×10^{-1}	1.57×10^{-1}	1.88×10^{-1}	4.98×10^{-1}	1.45
0.5	5.73×10^{-3}	1.27×10^{-2}	2.34×10^{-2}	2.99×10^{-2}	3.91×10^{-2}	3.17×10^{-2}	1.48×10^{-1}
1	6.58×10^{-4}	1.86×10^{-3}	4.41×10^{-3}	6.29×10^{-3}	9.48×10^{-3}	2.32×10^{-3}	2.08×10^{-2}
2	4.17×10^{-5}	1.72×10^{-4}	5.67×10^{-4}	9.67×10^{-4}	1.68×10^{-3}	9.64×10^{-5}	2.32×10^{-3}

As we see from these data E_1 and E_∞ differ by not more than a factor 2 or 3 when $x \ll 0.2$. At higher distances the differences are greater but the total energy of interaction is then already so small that the case is of little interest [7]).

In practical cases the energy will therefore mainly be fixed by the size of the smallest of the two particles, the size of the second particle having comparatively little influence.

It will further be noted that the energy (formula 11) is a function of x and y only; that means if we make both particles c times as large and put them c times as far apart the energy retains the same value. This result can be understood in a simple way which leads to a fundamental generalisation.

Consider (fig. 5*A*) two particles and two elements of volume dv_1 and dv_2 one in each particle. If the particles contain q atoms per cm^3 which interact with an energy λ/r^n the contribution to the total energy by the atoms in dv_1 and dv_2 will be

$$dE = \frac{\lambda\, q\, dv_1\, q\, dv_2}{r^n} \tag{4}$$

If we now increase all geometrical dimensions in the ratio c the contribution by the corresponding volume elements dv_1' and dv_2' in the new configuration (fig. 5*B*) will be

$$dE' = \frac{\lambda\, q\, dv_1'\, q\, dv_2'}{(r')^n} = \frac{\lambda\, q^2\, c^3\, dv_1\, c^3\, dv_2}{c^n\, r^n} = \frac{dE}{c^{n-6}}. \tag{5}$$

Since each elementary part of the energy has changed in the ratio $1/c^{n-6}$ the same will hold for the total energy.

Therefore, if we increase the size of the particles in the ratio c and put them c times as far apart the energy of interaction varies as $1/c^{n-6}$; the energy remains constant when $n = 6$, increases when $n < 6$ and decreases when $n > 6$.

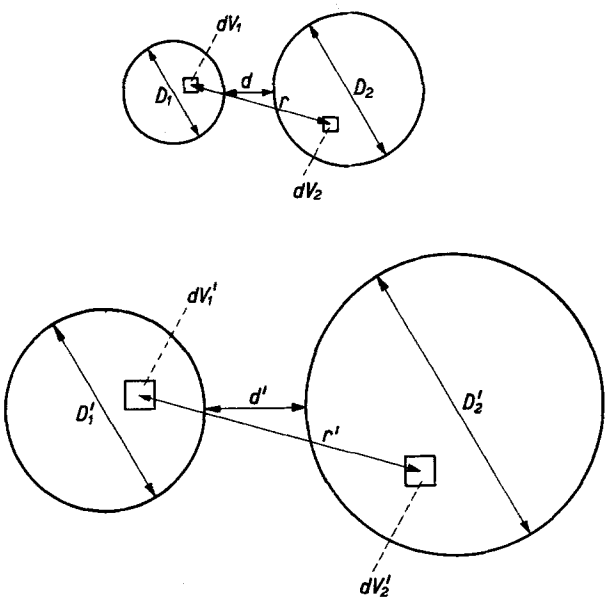

Fig. 5.

$D_1' = cD_1$, $d^1 = cd$, $dV_1' = c^3 dV_1$ etc.

This illustrates why the force of gravity which is negligibly small when acting between atoms or colloidal particles predominates when the particles attain the size of celestial bodies.

It is easily deduced that when the energy varies with the geometrical dimensions as $1/c^{n-6}$ the forces will very as $1/c^{n-5}$. Accordingly the force represented by formula (16) is not a function of x and y only; the diameter D_1 enters explicitly in the expression.

§ 4. *The constant A.* If two particles are embedded in a fluid and the London-van der Waals force between particlesand fluid is greater than between the particles themselves, it might be thought that the resultant action will be a repulsion rather than an attraction As has been pointed out to the author by Dr. J. H. de Boer, this

conclusion does not hold. Owing to a peculiar property of the London-van der Waals forces, the resultant force is generally attractive even when the particles are surrounded by fluid. This is a matter of considerable interest which warrants a detailed discussion.

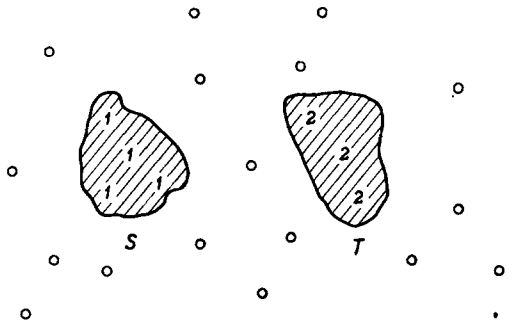

Fig. 6.

Consider (fig. 6) two particles S and T consisting of two different solid substances 1 and 2 and embedded in a fluid 0. In evaluating the energy variations in this system we have to take into account not only the two solid particles, which we may designate as S_1 and T_2, but also particles of the same size but consisting of the fluid 0; these will be described as particles S_0 and T_0.

Further we denote as:

E_{12} = the energy of interaction between the solid particles S_1 and T_2.

E_{10} = the energy of interaction between a solid particle S_1 with a fluid particle T_0.

E_{20} = the energy of interaction between a fluid particle S_0 and a solid particle T_2.

E_{00} = the energy of interaction between two fluid particles S_0 and T_0.

These energies will be functions of the distance between the particles.

Now, if E_1 represents the energy of a solid particle S_1 in the liquid at infinity, this particle when brought in the neighbourhood of the particle T_2 will possess an energy $E_1 + E_{12} - E_{10}$. But, while bringing S_1 towards T_2, we have at the same time to remove a particle S_0 towards infinity. To this will correspond a change in energy from $E_0 + E_{20} - E_{00}$ to E_0 when E_0 is the energy of the particle S_0 at infinity. Since E_1 and E_0 are constants the energy changes attendant to variations in the distance between the particle S_1 and T_2 will be:

$$E = E_{12} - E_{10} - (E_{20} - E_{00}) = E_{12} + E_{00} - E_{10} - E_{20} \quad (23)$$

This expression is as yet entirely independent of the nature of the forces of interaction. It is, however, inherent to our argument that the energy of interaction of one particle with the fluid shall be unaffected by the presence or absence of the other particle. This is a serious limitation, which will be violated as soon as the interaction between particles and fluid is accompanied by an orientation of the fluid molecules; for the degree of orientation with respect to T_2 will certainly be influenced by the presence of the particle S_1 [8])

In such cases we may generally consider the total energy to be made up of two parts: 1. a part independent of the orientation of the fluid molecules and 2. an additional amount due to this orientation. Whenever the latter part is only a small fraction of the total, we are still entitled to assume that conclusions drawn from equation (23) will in the main be correct. The use of (23) must be restricted to such cases.

Let us now apply (23) to London-van der Waals forces. In § 2 and 3 the energy between two spherical particles in vacuo was expressed as:

$$E = -A\, E_y(x) \tag{24}$$

where $E_y(x)$ is a function of the geometrical data (diameters and distance) only and

$$A = \pi^2 q^2 \lambda \tag{25}$$

q being the number of atoms per cm^3 and λ the London-van der Waals constant.

If the two particles are composed of two different substances 1 and 2 we have obviously to take:

$$A = \pi^2 q_1 q_2 \lambda_{12} \tag{26}$$

And if these two particles are embedded in a fluid 0 (23) proves that (24) is still valid provided we assign to A the value

$$A = \pi^2 \{q_1 q_2 \lambda_{12} + q_0^2 \lambda_{00} - q_0 q_1 \lambda_{01} - q_0 q_2 \lambda_{02}\} \tag{27}$$

the q's being atom densities and the λ's London-van der Waals constants for the pairs of atoms indicated by the suffix.

Now λ is approximately expressed by [9])

$$\lambda_{kl} = \frac{3}{2} \alpha_k \alpha_l \frac{I_k I_l}{I_k + I_l} \tag{28}$$

where α_k and α_l are the polarisabilities, I_k and I_l certain characteristic potentials of the atoms.

Inserting (28) in (27) and writing for the sake of simplicity:

$$\alpha_0 q_0 I_0 = \mu_0 \quad \alpha_1 q_1 I_1 = \mu_1 \text{ etc.} \tag{29}$$

we get

$$A = \frac{3\pi^2}{2}\left\{\frac{\mu_1\,\mu_2}{I_1+I_2} + \frac{\mu_0^2}{2I_0} - \frac{\mu_0\,\mu_1}{I_0+I_1} - \frac{\mu_0\,\mu_2}{I_0+I_2}\right\} \tag{30}$$

For two particles of the same substance we have $\mu_1 = \mu_2$, $I_1 = I_2$ and

$$A = \frac{3\pi^2}{2}\left\{\frac{\mu_1^2}{2I_1} + \frac{\mu_0^2}{2I_0} - \frac{2\mu_0\,\mu_1}{I_0+I_1}\right\} =$$

$$= \frac{3\pi^2}{2}\left\{\frac{I_0\,I_1\,(\mu_0-\mu_1)^2 + (\mu_0\,I_1 - \mu_1 I_0)^2}{2I_0\,I_1(I_0+I_1)}\right\}. \tag{31}$$

Since I_0 and I_1 are essentially positive, A will be positive, which means that the force is always an attraction [10]).

If the particles do not consist of the same material, this need no longer be true. Putting for instance in (30) $I_0 = I_1 = I_2$ and $\mu_0 = \frac{1}{2}(\mu_1 + \mu_2)$ we obtain a negative value.

Above the particles and the fluid were taken to contain each but one kind of atoms. If they consist of more than one component, the results can be generalised; for particles of the same composition A is essentially positive. The proof which requires a somewhat tedious mathematical argument is given separately in an appendix.

Recapitulating we have:

The London-van der Waals forces between two particles of the same material embedded in a fluid is always attractive, provided there is no marked orientation of the fluid molecules. If the particles are of different composition, the resultant force may be a repulsion.

The actual value of the constant A will vary from case to case. Calculating q, the atom densities, for some substances, we find

q	q	q
Ag 59×10^{21} Au 60×10^{21}	AgJ 30×10^{21} As_2S_3 42×10^{21}	SiO_2 80×10^{21} Fe_2O_3 97×10^{21}

which shows that q will be of the order 50×10^{21}. For the alkalihalides the value of the London-van der Waals constant has been computed by Mayer [11]). He obtains a maximum value $\lambda = 400 \times 10^{-60}$ erg cm^6 for two iodine ions. On the average, however, λ is less

and of the order 100×10^{-60} erg cm^6; 1×10^{-60} erg cm^6 is definitely a low value. Values of the same order of magnitude have recently been published by London [12]).

Using these data to calculate $A = \pi^2 q^2 \lambda$ we get:

$A = 3 \times 10^{-12}$ erg as a very high value

$A = 0.7 \times 10^{-12}$ erg as an average value

and $A = 0.7 \times 10^{-14}$ erg as an abnormally low value.

When the particles are embedded in a fluid, A will be of the same order, though somewhat smaller, being now the difference between positive and negative terms.

Generalising, A may be assumed to vary between 10^{-14} and 10^{-11} erg as extreme limits and to lie between 10^{-13} and 10^{-12} erg in most cases. On this basis the magnitude of London-v. d. Waals forces in colloidal systems will be discussed in a subsequent paper.[1])

APPENDIX.

General proof that the forces between two particles of the same composition are always attractive.

First suppose the surrounding fluid to be composed of only one kind of atoms and let the particles contain n different kinds of atoms with atom densities $q_1, q_2 \ldots . q_n$. To find A, every component of the first particles must be combined with every component of the second particle according to equation (30) and these expressions must be summed. We then get:

$$A = \frac{3\pi^2}{2} \sum_1^n{}_k \sum_1^n{}_l \left\{ \frac{\mu_k \mu_l}{I_k + I_l} + \frac{\mu_0^2}{2I_0} - \frac{\mu_0 \mu_k}{I_0 + I_k} - \frac{\mu_0 \mu_l}{I_0 + I_l} \right\} \quad (32)$$

or

$$A = \frac{3\pi^2}{2} \left\{ \sum_1^n{}_k \sum_1^n{}_l \frac{\mu_k \mu}{I_k + I_l} + \frac{n^2 \mu_0^2}{2I_0} - 2n \mu_0 \sum_1^n{}_k \frac{\mu_k}{I_0 + I_k} \right\}. \quad (33)$$

After introducing a new set of variables

$$\beta_0 = -n\mu_0 \qquad \beta_1 = \mu_1 \qquad \beta_k = \mu_k$$

equation (33) can be written:

$$\frac{2A}{3\pi^2} = \left\{ \sum_0^n \frac{\beta_k^2}{2I_k} + 2 \sum_0^n{}_k \sum_{k+1}^n{}_l \frac{\beta_k \beta_l}{I_k + I_l} \right\} = \left\{ \frac{\beta_0^2}{2I_0} + \frac{\beta_1^2}{2I_1} \ldots . + \frac{\beta_n^2}{2I_n} + \right.$$

$$\left. + \frac{2\beta^0 \beta_1}{I_0 + I_1} + \frac{2\beta_0 \beta_2}{I_0 + I_2} + \ldots . + \frac{2\beta_1 \beta_2}{I_1 + I_2} + \frac{2\beta_1 \beta_3}{I_1 + I_3} + \ldots . + \frac{2\beta_{n-1} \beta_n}{I_{n-1} + I_n} \right\}. \quad (34)$$

All the I's are essentially positive. A will therefore always be positive, if it can be proved that for positive I's the expression (34) is a positive quadratic form in the β's.

Splitting off a square in the usual way, we find:

$$\frac{2A}{3\pi^2} = \frac{1}{2I_0}\left\{\beta_0 + \frac{2I_0}{I_0+I_1}\beta_1 + \frac{2I_0}{I_0+I_2}\beta_2 + \cdots \frac{2I_n}{I_0+I_n}\beta_n\right\}^2 +$$
$$+ \frac{\beta_1^2}{2I_1}\left(\frac{I_0-I_1}{I_0+I_1}\right)^2 + \frac{\beta_2^2}{2I_2}\left(\frac{I_0-I_2}{I_0+I_2}\right)^2 + \cdots + \frac{\beta_n^2}{2I_n}\left(\frac{I_0-I_n}{I_0+I_n}\right)^2 +$$
$$+ \frac{2\beta_1\beta_2}{I_0+I_2}\left(\frac{I_0-I_1}{I_0+I_1}\right)\left(\frac{I_0-I_2}{I_0+I_2}\right) + \frac{2\beta_1\beta_3}{I_0+I_3}\left(\frac{I_0-I_1}{I_0+I_1}\right)\frac{I_0-I_3}{I_0+I_3}\Big) +$$
$$+ \cdots + \frac{2\beta_{n-1}\beta_n}{I_{n-1}+I_n}\left(\frac{I_0-I_{n-1}}{I_0+I_{n-1}}\right)\left(\frac{I_0-I_n}{I_0+I_n}\right). \quad (35)$$

as is easily verified.

Writing:

$$\gamma_k = \beta_k \frac{I_0 - I_k}{I_0 + I_k}$$

the last equation reduces to:

$$\frac{2A}{3\pi^2} = \frac{1}{2I_0}Q^2 + \frac{\gamma_1^2}{2I_1} + \frac{\gamma_2^2}{2I_2} + \cdots + \frac{\gamma_n^2}{2I_n} +$$
$$+ \frac{2\gamma_1\gamma_2}{I_1+I_2} + \frac{2\gamma_1\gamma_3}{I_1+I_3} + \cdots + \frac{2\gamma_{n-1}\gamma_n}{I_{n-1}+I_n} \quad (36)$$

where

$$Q = \beta_0 + \frac{2I_0}{I_0+I_1}\beta_1 + \frac{2I_0}{I_0+I_2}\beta_2 + \cdots + \frac{2I_0}{I_0+I^n}\beta_n. \quad (37)$$

By (36) expression (34) is written as the sum of a positive term $Q^2/2I_0$ and an expression of the same nature as (34) but with one variable less. Consequently, if (34) is a positive quadratic form for n variables, the same is true for $n+1$ variables and since it has been demonstrated for $n = 1$ (see page 012) (34) is a positive quadratic function of the β's for any number of variables.

If the fluid consists of more than one component, A will be the sum of a number of expressions (32), one for each component. Since these are separately positive, the same will hold true for their sum.

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1) H. C. Hamaker, London-van der Waals forces in colloidal systems, to appear shortly in Rec. Trav. Chim. des Pays-Bas
2) R. S. Bradley, Phil. Mag. **13**, 853, 1932.
3) The last formula on page 856.
4) Writing (13*b*) in terms of d, D_1, D_2 etc. and differentiating with respect to d, we find a force:

$$F = \frac{\pi^2 q^2 \lambda}{12} \frac{D_1 D_2}{D_1 + D_2} \frac{1}{d^2} . \qquad (13c)$$

This is Bradley's final result (*l.c.* p. 856 form. 4). Bradley based his calculations on a force λ/r^n to which corresponds an energy $\lambda/(n-1)\, r^{(n-1)}$. To obtain the above expression we have therefore in Bradley's equation to replace $\lambda/n - 1$ by λ and to take $n = 7$.
5) M. Polanyi and F. London, Naturwissenschaften **18**, 1099 1930.
6) This formula has in a slightly different way been derived by J. H. de Boer. See Trans. Faraday Soc. **32**, 21 (1936).
7) Compare the paper announced in note 1.
8) Besides London-van der Waals forces are due to polarisation of the atom. If the forces are strong the polarisation with respect to one particle will influence the polarisability with respect to the second particle. In this respect equation (25) must be considered as a first approximation.
9) F. London, Z. physik. Chem. *B* **11**, 246 (1936).
10) Compare Trans. Faraday Soc. **32**, 118 (1936), where J. H. de Boer discusses the analogous question for two atoms immersed in a liquid.
11) J. E. Mayer, J. chem. Physics I, 278, 1933.
12) F. London, Trans. Faraday Soc. **33**, 19, 1937.