

the force law $F(r)$ between them by

$$F(r) = -dw(r)/dr = -nCm_1m_2/r^{n+1}, \quad (1.1)$$

where m_1, m_2 are the molecular masses, r their separation, C a constant, and n some integer believed to be 4 or 5, which may be compared with $n = 1$ for the gravitational interaction:

$$w(r) = -Gm_1m_2/r, \quad G = 6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}. \quad (1.2)$$

It is instructive to see how the power-law index n was so chosen. It arose from an appreciation of the fact that if intermolecular forces are not to extend over large distances, the value of n must be greater than 3. Why this is so can be simply established as follows: suppose the attractive potential between two molecules or particles to be of the general form $w = -C/r^n$, where n is an integer. Now consider a region of space where the number density of these molecules is ρ . This region can be a solid, a liquid, a gas, or even a region in outer space extending over astronomical distances. Let us add all the interaction energies of one particular molecule with all the other molecules in the system. The number of molecules in a region of space between r and $(r + dr)$ away will be $\rho 4\pi r^2 dr$ (since $4\pi r^2 dr$ is the volume of a spherical shell of radius r and thickness dr , i.e., of area $4\pi r^2$ and thickness dr). The total interaction energy of one molecule with all the other molecules in the system will therefore be given by

$$\begin{aligned} \text{total energy} &= \int_{\sigma}^L w(r) \rho 4\pi r^2 dr = -4\pi C \rho \int_{\sigma}^L r^{2-n} dr \\ &= \frac{-4\pi C \rho}{(n-3)\sigma^{n-3}} \left[1 - \left(\frac{\sigma}{L}\right)^{n-3} \right] \\ &= -4\pi C \rho / (n-3)\sigma^{n-3} \quad \text{for } n > 3 \quad \text{and } L \gg \sigma, \end{aligned} \quad (1.3)$$

where σ is the diameter of the molecules and L is the size of the system (e.g., the dimensions of a solid or the size of the box containing a gas). We can see that since σ must be smaller than L (i.e., $\sigma/L < 1$), large distance contributions to the interaction will disappear only for values of n greater than 3 (i.e., for $n = 4, 5, 6, \dots$). But for n smaller than 3, the second term in Eq. (1.3) will be greater, and the contribution from more distant molecules will dominate over that of nearby molecules. In such cases the size of the system must be taken into account, as occurs for the gravitational force where

$n = 1$ and where distant planets, stars, and even galaxies are still strongly interacting with each other (see Problem 1.2).

In later chapters we shall see that theoretical derivations of intermolecular force potentials do indeed predict that n always exceeds 3 asymptotically, and it is for this reason that the bulk properties of solids, liquids and gases do not depend on the volume of material or on the size of the container (unless these are extremely small) but only on the forces between molecules in close proximity to each other. Important long-range intermolecular forces also exist, especially between macroscopic particles and surfaces, but their effective range of action rarely exceeds 100 nm.

Returning to the latter part of the nineteenth century, hopes for an all-embracing force law dwindled as it became increasingly apparent that no suitable candidate would be forthcoming to explain the multitude of

1.3 EARLY SCIENTIFIC PERIOD: CONTRASTS WITH GRAVITATIONAL FORCES

In the seventeenth century our subject entered its first phase of scientific scrutiny. Newton considered how the forces between molecules could be linked to the physical properties of matter, and later a number of eighteenth century researchers investigated the phenomenon of the capillary rise of liquids in glass tubes. In 1808 Clairaut suggested that capillarity could be explained if the attraction between the liquid and glass molecules was different from the attraction of the liquid molecules for themselves. It was also noticed that the height of rise of a liquid column does not depend on the capillary wall thickness, which led to the conclusion that these forces must be of very short range (or, in the language of the time, extended over 'insensible' distances).

During the nineteenth century it was believed that one simple universal force law (similar to Newton's law for the gravitational force) would eventually be found to account for all intermolecular attractions. To this end a number of interaction potentials were proposed that invariably contained the masses of the molecules, attesting to the belief at the time that these forces are related to gravitational forces. Thus, typical *interaction potentials* of two molecules were of the form $w(r) = -Cm_1m_2/r^n$, which is related to

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Intermolecular and
Surface Forces

Note: the integral in step ⑥ is not easily calculated; it would be very labour intensive to do so, and not even Mathematica is a big help.

Note: a concise derivation for the case of two spheres with different radii is given by Hamaker, *Physica IV*, p.1058-1072 (1937).

We can write the result of step ⑥ as:

$$\text{with } x = \frac{h}{a}$$

$$U = -\frac{A}{6} \left\{ \frac{2}{x(x+4)} + \frac{2}{(x+2)^2} + \ln \left(1 - \frac{4}{(x+2)^2} \right) \right\}$$

which shows that U is dependent on $x = \frac{h}{a}$.

Note: the original Hamaker paper states for 2 spheres with radii R_1 and R_2 respectively, a center-to-center distance C apart:

$$U = -\frac{\pi^2 q^2 \lambda}{6} \left\{ \frac{2R_1 R_2}{C^2 - (R_1 + R_2)^2} + \frac{2R_1 R_2}{C^2 - (R_1 - R_2)^2} + \ln \frac{C^2 - (R_1 + R_2)^2}{C^2 - (R_1 - R_2)^2} \right\}$$

If we take $R_1 = R_2$ we can write:

$$U = -\frac{\pi^2 q^2 \lambda}{12} \left\{ \frac{4R^2}{C^2 - (4R^2)} + \frac{4R^2}{C^2 - 0} + 2 \ln \frac{C^2 - 4R^2}{C^2} \right\}$$

And if we now take $x = C/2R$ the reduced center-to-center distance, we arrive at formula (19) from the lecture notes:

$$U = -\frac{A_{12}}{12} \left\{ \frac{1}{x^2 - 1} + \frac{1}{x^2} + 2 \ln \frac{x^2 - 1}{x^2} \right\} \quad (\text{Note } C > 2R !)$$

Returning to the definition $x = \frac{h}{a}$ as before, we can expand the expression of step ⑥ in a Taylor series (with Mathematica):

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In[34]:= Series[2/(x*(x+4)) + 2/((x+2)^2) + Log[(1 - (4/((x+2)^2)))] , {x, 0, 1}]
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out[34]= 1/(2x) + (3/8 + Log[x]) - 39x/32 + O[x]^2
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Although $\frac{1}{2x} \rightarrow +\infty$ and $\ln(x) \rightarrow -\infty$ if $x \downarrow 0$, the expression can be approximated as $\frac{1}{2x}$ (for $x = \frac{h}{a} \ll 1$), as becomes obvious from the following two plots:

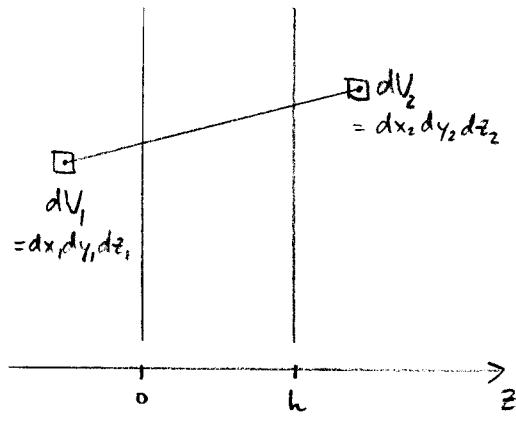
④ Hamaker on two infinite half-spaces:

Method:
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Foundations of
Colloid Science

Equation (17):
$$dU_{12} = \frac{-C_{12} \rho_1 \rho_2 dV_1 dV_2}{\left\{ (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \right\}^3}$$

①

②



with $H_{12} = \pi C_{12} \rho_1 \rho_2$:

$$U_{12} = -\frac{H_{12}}{\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_h^0 \frac{dx_1 dx_2 dy_1 dy_2 dz_1 dz_2}{\left\{ (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \right\}^3}$$

Substitute: $x = x_2 - x_1$ $y = y_2 - y_1$
 $x' = x_2 + x_1$ $y' = y_2 + y_1$

and integrate over x' and y' (which gives an area):

$$\frac{U_{12}}{\text{area}} = -\frac{H_{12}}{\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_h^0 \frac{dx dy dz_1 dz_2}{\left\{ x^2 + y^2 + (z_2 - z_1)^2 \right\}^3}$$

With cylindrical coordinates

$r^2 = x^2 + y^2$, Jacobian = r

$$\begin{aligned} \frac{U_{12}}{\text{area}} &= -\frac{H_{12}}{\pi^2} \int_0^{\infty} \int_{-\infty}^{\infty} \int_h^0 \frac{2\pi r dz_1 dz_2 dr}{\left\{ r^2 + (z_2 - z_1)^2 \right\}^3} = -2 \frac{H_{12}}{\pi} \left[\frac{1}{2} \int dz \right] \int_0^{\infty} \frac{dr^2}{(r^2 + z^2)^3} = -\frac{H_{12}}{\pi} \left[\frac{1}{2} \int dz \right] \left[\frac{1}{(r^2 + z^2)^2} \right]_0^{\infty} \\ &= \frac{H_{12}}{2\pi} \int_{-\infty}^{\infty} dz_1 \int_h^{\infty} dz_2 \frac{1}{(z_2 - z_1)^4} = \frac{H_{12}}{6\pi} \int_h^{\infty} dz_2 \frac{1}{z_2^3} = -\frac{H_{12}}{12\pi} \cdot \frac{1}{h^2} \end{aligned}$$

3) A permanent dipole with induced dipole

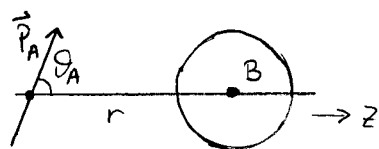
$$\vec{p}_B = \alpha_B \vec{E} \quad \text{with} \quad \vec{E} = \vec{E}_A$$

$$U = - \int_0^{\vec{E}} \vec{p}_B \cdot d\vec{E}_A = -\frac{1}{2} \alpha_B E_A^2 \quad \text{Note: we are considering an induced dipole!}$$

$$\text{but } \vec{E}_A = \vec{E}_{\text{dipole}} = \frac{1}{4\pi\epsilon_0 r^3} [3(\vec{p} \cdot \hat{r})\hat{r} - \vec{p}]$$

$$\begin{aligned} \text{So: } E_A^2 &= \vec{E}_A \cdot \vec{E}_A = \frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \left\{ [3(\vec{p} \cdot \hat{r})\hat{r} - \vec{p}] \cdot [3(\vec{p} \cdot \hat{r})\hat{r} - \vec{p}] \right\} \\ &= \frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \left\{ 9(\vec{p} \cdot \hat{r})^2 - 3(\vec{p} \cdot \hat{r})(\vec{p} \cdot \hat{r}) - 3(\vec{p} \cdot \hat{r})(\vec{p} \cdot \hat{r}) + (\vec{p} \cdot \vec{p}) \right\} \\ &= \frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \left\{ 3(\vec{p} \cdot \hat{r})^2 + (\vec{p} \cdot \vec{p}) \right\} \end{aligned}$$

$$\text{where } \vec{p} \cdot \hat{r} = p_A \cos\vartheta_A \quad \text{and} \quad \vec{p} \cdot \vec{p} = p_A^2$$



$$\rightarrow U = -\frac{1}{2} \alpha_B \frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} p_A^2 (1 + 3\cos^2\vartheta_A)$$

B

$$\langle \cos^2\vartheta \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \cos^2\vartheta \sin\vartheta d\vartheta = -\frac{1}{6} [\cos^3\vartheta]_0^\pi = \frac{1}{3}$$

$$\rightarrow \langle U \rangle = -\frac{1}{2} \alpha_B \frac{1}{(4\pi\epsilon_0)^2} \frac{1}{r^6} p_A^2 (1 + 3 \cdot \frac{1}{3}) = -\frac{\alpha_B p_A^2}{(4\pi\epsilon_0)^2 r^6}$$

Note: ① induced dipole is parallel to permanent dipole

② we need a rotational average ($\langle \cos^2\vartheta \rangle = \frac{1}{3}$) and not the Boltzmann averaging of the previous exercise

9 a

We combine the results of exercise 5b and 8 to get:

$$V(h) = 8 k_B T \frac{a}{l_B} t_0^2 e^{-\kappa h} - \frac{Aa}{12h} \quad \text{for } \frac{h}{a} \ll 1.$$

The condition for an extremum is $\frac{dV}{dh} = 0$;

$$\frac{Aa}{12h^2} - 8 k_B T \frac{a}{l_B} t_0^2 \kappa e^{-\kappa h} = 0$$

Now substitute $y = \kappa h$, then $\kappa e^{-y} = \frac{Al_B}{96 k_B T t_0^2 h^2}$

$$\text{thus } h^2 \kappa^2 e^{-y} = y^2 e^{-y} = \frac{Al_B \kappa}{96 k_B T t_0^2}$$

Consider the function $f(y) = y^2 e^{-y}$.

Then $\frac{df}{dy} = 2y e^{-y} - y^2 e^{-y}$. So, $f(y)$ has an extremum if

$$\frac{df}{dy} = 0 \rightarrow 2y e^{-y} - y^2 e^{-y} = 0$$

$$(2y - y^2) e^{-y} = 0$$

$$y(2-y) e^{-y} = 0 \rightarrow y=0 \text{ or } y=2.$$

$$\frac{d^2f}{dy^2} = e^{-y}(2-4y+y^2)$$

So, $\left. \frac{d^2f}{dy^2} \right|_{y=2} = -2e^{-2} < 0$, thus $f(y)$ has a maximum at $y=2$.

For $y=2$ (that is, $h = 2\kappa^{-1}$) we have $f(2) = 4e^{-2} \approx 0.541$.

Since the condition $\frac{dV}{dh} = 0$ is equivalent to the condition

$$y^2 e^{-y} = \frac{Al_B \kappa}{96 k_B T t_0^2}, \text{ this implies that there can only}$$

be an extremum in $V(h)$ if $\frac{Al_B \kappa}{96 k_B T t_0^2} \leq 4e^{-2}$.

This will happen for:

- * low Hamaker constants, i.e. small London-Vander Waals attractions
- * low κ , i.e. low salt concentrations
- * high t_0 , i.e. high surface potential

b

Example: $A = 20 \cdot 10^{-20} \text{ J } (\approx 50 \text{ kT})$

$\kappa^{-1} = 10 \cdot 10^{-9} \text{ m } (10^{-3} \text{ M of 1-1 electrolyte in } H_2O, \epsilon = 80).$

$$t_0^2 > \frac{Al_B \kappa}{96 k_B T (4/e^2)} \quad l_B = 7.13 \text{ \AA}$$

$$t_0^2 > 0.0678 \rightarrow t_0 > 0.26 \rightarrow \phi_0 = 4 \tanh^{-1}(0.26) = 1.07$$

$$\psi_0 = \frac{kT}{e} \phi_0 = 27 \text{ mV.}$$