Adhesion, Molecular Interaction, and Surface Roughness

5. Molecular Interaction with Small Clearances between Contiguous Bodies

The clearance, i.e., the distance between contiguous bodies, in either particle adhesion or film adhesion, if there is no layer of liquid between the solid bodies, may amount to several molecular diameters. If the contiguous bodies are separated by a liquid layer, the distance between them may be several hundred molecular diameters. Similarly large distances between a particle and a surface may be found when the surfaces of both bodies are rough.

The magnitude of the clearance between the adherent particles and the surface determines the specific features of molecular interaction of the contiguous bodies. First, let us examine the molecular interaction when the clearance between two ideally smooth mating surfaces is no more than a few molecular diameters. The energy of interaction between two molecules \( i \) and \( j \) located at a distance \( H \) can be calculated in accordance with the equation [39]

\[
E_{i,j} = -\frac{\lambda_{i,j}}{H^6}
\]  

(II.1)

where \( \lambda_{i,j} \) is the constant characterizing the orientation (\( \lambda_{i,j}^o \)), induction (\( \lambda_{i,j}^i \)), and dispersion (\( \lambda_{i,j}^d \)) interaction:

\[
\lambda_{i,j} = \lambda_{i,j}^o + \lambda_{i,j}^i + \lambda_{i,j}^d
\]  

(II.2)

The minus sign in Eq. (II.1) conventionally designates energy of attraction.

Calculations show that the induction and orientation effects are insignificant and may be neglected, particularly for condensed bodies. Then \( \lambda_{i,j} = \lambda_{i,j}^d \), and \( \lambda_{i,j}^d \) can be determined from the formula
where \( h \) is Planck's constant; \( \nu_i \) and \( \nu_j \) are the vibration frequencies of the interacting electronic oscillators; \( \alpha_i \) and \( \alpha_j \) are the polarizabilities of the molecules \( i \) and \( j \).

The characteristic feature of dispersion (London) forces is their additivity. A molecule induces periodic dipoles in several neighboring molecules. The induced dipole is attracted to the original dipole. In this connection, the energy of attraction between two solids may be regarded as the sum of the energies of attraction between the corresponding pairs of molecules making up the particular solid bodies.

Strictly speaking, dispersion interaction is valid only for two highly rarefied systems, i.e., gages. Extension of the principal of additivity of forces to condensed systems that do not represent a simple sum of free molecules has not yet been justified by theory. The experimental value found by Bradley [25] for the force on interaction between two quartz and borate spheres, however, was close to the value calculated on the basis of his assumption of additivity of molecular interaction. Hence, we may a priori accept the additivity of London interaction and extend this principal to condensed systems since at the present time there are no other methods for evaluating molecular interaction of such bodies when they are separated by a small gap.

A conversion from the energy of interaction of molecules to the energy of interaction of condensed systems was given by Hamaker [39].

The energy of interaction between elementary volumes of two spherical particles (Fig. II.1.a) containing \( n \) molecules per \( \text{cm}^3 \) is, when Eq. (II.1) is taken into account,

\[
E = - \int_{V_1} dV_1 \int_{V_2} \left( n^2 \lambda_i, j / H^6 \right) dV_2
\]

where \( \lambda_i, j \) is the London constant; \( H \) is the distance between the molecules; \( V_1 \) and \( V_2 \) are the total volumes of the two spheres.

The integration of Eq. (II.4) is cumbersome, and there is no point in carrying it out completely. Here we need only give an idea of the integration and the way in which the power of \( H \) is reduced when we go from interaction between molecules to interaction between condensed bodies. We will locate one molecule

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\[
\lambda_{i, j}^d = - \frac{3}{2} h \left[ \nu_i \nu_j / (\nu_i + \nu_j) \right] \alpha_i \alpha_j
\]

(II.3)