Possible studies on adhesion in space

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Abstract. This paper reviews possible experiments on adhesion that can be carried out in a space lab environment. After introducing the basic concepts of adhesion physics, the proposed European experiment on surface energy measurement by dynamic methods in space environment is discussed and reviewed. It is concluded that as of now more studies on adhesion in terrestrial environment are desirable than space experiments.

Keywords. Adhesion; surface energy; space experiments.

“"There are agents in Nature able to make particles of joint stick together by very strong attractions, and it is the business of experimental philosophy to find them out”

—Newton

1. Introduction

This paper will deal with possible studies pertaining to adhesion which can be carried out in Spacelab-like environment. Our concern will be mainly with the basic aspects of the phenomenon of adhesion, and related questions pertaining to surface physics. However, it may be pertinent to begin with a brief discussion of how adhesives are used in space technology. This will provide, though perhaps tenuously, some justification for engaging in basic studies!

2. Adhesives in space technology

The ASTM Bulletin defines adhesion as “the state in which two surfaces are held together by interfacial forces”. An adhesive is a material that binds two surfaces by surface attachment.

For many years, adhesives had limited use in aircraft and spacecraft. The Apollo spacecraft was the first large airborne vehicle in which adhesives were utilised throughout most of the load-bearing structure. In the initial stages, there were many problems. Most of the bonds had to be scrapped or reworked due to voids caused by volatile matter escaping during the cure of adhesives. This led to a programme for developing stable, high-temperature adhesives, free from volatile formation.

The basic strategy was to try and introduce a stabilising linkage in the main chain of the epoxy monomer (Spiker and Barnes 1970). The chemical group...
selected for this purpose was carborane \( \text{C}_2\text{B}_{10}\text{H}_{12} \). The carbon and the boron atoms in carborane are arranged in an isocahedral array, and three isomers, ortho, meta and para, are possible, depending on the location of the carbon atoms. In orthocarborane, the two carbon atoms are adjacent to each other, and have a strong electron-withdrawing characteristic. Consequently, when this unit is bonded to other groups, the chemistry of these other groups is strongly affected. The structure of the substituted carborane is represented by

\[
\begin{array}{c}
\text{R} - \text{C} - \text{C} - \text{R} \\
\big/ \text{O} \\
\text{B}_{10}\text{H}_{12}
\end{array}
\]

where \( R \) belongs to the epoxy. The monomer properties are substantially altered by bonding to carborane, and overall improved stability results. Incidentally we see here basic science in action to solve a practical problem.

3. Surface energy

We now address ourselves to the subject proper, and begin with a consideration of a crucial quantity, namely, the specific surface free energy. Denoted by \( \gamma \), it is often abbreviated simply as surface energy. It is defined as the isothermal reversible work required for creating 1 cm\(^2\) of a new surface. We can, for example, visualise this surface to be produced by applying a tension on a long prism with a square cross-section, and having a 1 cm edge. Further, the breaking is assumed to be done in a perfect vacuum. Since an energy \( \gamma \) is associated with each of the two surfaces created, it is evident by a converse argument that, if the solid could be restored to its original condition by a perfect adhesion of the two surfaces, the energy gained would be \( 2\gamma \).

Observe that \( \gamma \) is essentially a macroscopic quantity. Though a tensor, we shall treat it here as a scalar. It is a convenient measure of surface properties, and fingerprints the latter the same way the yield stress, for example, gives a comprehensive feel for the mechanical properties of materials.

The calculation of \( \gamma \) from first principles has attracted considerable attention especially for atoms interacting via dispersion forces. We remind ourselves that such forces are operative mainly for closed-shell atoms.

The physical origin of these forces is schematically illustrated in figure 1. Here it is assumed that the interaction is instantaneous, i.e., there is no delay in the inducing of a dipole moment on atom 2 due to a fluctuation in atom 1. Clearly this is not valid, especially for large \( r \), since signals cannot travel faster than the velocity of light \( c \). Retardation effects thus set in for large separations, and must be allowed for.

The force we have been considering so far is that between isolated atoms. As far as adhesion is concerned, we need to know something about forces between bodies with surfaces. These forces can be calculated by superposing the forces between all distinct pairs of atoms, one each in the two bodies. Table 1 (Israelachivili and Tabor 1972) gives a feel for such forces for different geometries.
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Interaction energy:

$$E = \frac{\mu_1 \mu_2}{r^3}$$

$$= \frac{\alpha_1^2 \alpha_2^2}{r^6}$$

Figure 1. Origin of dispersion forces. (a) depicts two closed-shell atoms in their respective ground states. A momentary fluctuation of charge in 1 can lead to an electric dipole moment as in (b). This dipole could then induce another in atom 2 as sketched in (c). The interaction energy goes as $r^{-6}$. The constant is roughly given by $\alpha_0 \alpha_1$, where $\alpha_0$ is the Bohr radius and $\alpha_1$ the atomic polarizability.

Table 1. Forces of relevance to adhesion.

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<th>Non retarded</th>
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<tr>
<td><img src="image" alt="Diagram" /></td>
<td>$F = \frac{\text{Const}}{d^{n}}$</td>
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To see the connection with $\gamma$, let us suppose that the atoms interact via the Lennard-Jones (LJ) potential

$$v(r) = 4\epsilon \left( (\sigma/r)^{12} - (\sigma/r)^6 \right),$$  \hfill (1)

where $\epsilon$ and $\sigma$ are constants. The former is related to the potential well depth and the latter to the hard-core radius of the interacting atom. We recall that the Lennard-Jones potential is a phenomenological two-body potential which incorporates, besides the repulsion, an attraction having the same form as that arising from dispersion.

Referring now to figure 2, if $\sigma(z)$ denotes the force between the two surfaces when the separation is $z$, then

$$\Delta F = -2\gamma = -\int_{z_0}^{\infty} \sigma(z) \, dz,$$

where $z_0$ is the equilibrium separation. For the LJ potential,

$$z_0 = (2/15)^{1/6}\sigma,$$

and

$$\sigma(z) = \frac{c}{z^6} \left[ 1 - (z_0/z)^2 \right],$$

where

$$c = \frac{1}{2} \left( \frac{4\pi\rho \sigma^4 n^2}{} \right),$$

$n$ being the density of the solid. On carrying through the integration, it is found

$$\gamma = 3c/16\epsilon\sigma^2.$$

This exercise, though elementary, gives a feel for how surface energy is calculated from basic considerations. The same technique can be applied to solids with other types of bonding, e.g., ionic, covalent, etc. Table 2 gives some results for ionic crystals (Gregg 1965) which, though outdated, are good enough to convey a feel for the magnitudes involved.

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**Figure 2.** Schematic drawing to illustrate the calculation of $\gamma$. When the separation between the surfaces is $z$, the force of attraction is $\sigma(z)$. $\gamma$ is obtained by calculating the work required to take the two surfaces from their equilibrium separation $Z_0$ to infinity.
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Table 2. Surface energies for some ionic crystals.

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<th>NaCl</th>
<th>NaBr</th>
<th>KCl</th>
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<tbody>
<tr>
<td>Plane</td>
<td>100</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>$\gamma$ (calc)</td>
<td>189</td>
<td>445</td>
<td>177</td>
</tr>
<tr>
<td>$\gamma$ (expt)</td>
<td>190</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: (1) $\gamma$ is quoted in erg cm$^{-2}$.
(2) The calculated values are for 0$^\circ$K, and reproduced from Gregg (1965).
(3) The experimental value quoted for NaCl is derived from surface tension measurements made above the melting point. This value has been extrapolated to 0$^\circ$K. This number also has been derived from Gregg.

For many years, surface forces were calculated only for atoms interacting, via dispersion forces. Lately calculations for other kinds of solids, including metals have started appearing. All these involve complications of their own. For instance, for metals one has to worry about the role played by the electron gas. Similarly, for covalent crystals, one has to reckon with bond-bending forces and so on. An additional complication is that in some cases, the surface layer has a different structure as compared to those beneath; this has been revealed by LEED experiments.

4. Concerning roughness

Implicit in the above analysis is the assumption that the surface is smooth, down to the atomic level. In practice this is not the case, and one rather has the situation depicted in figure 3.

This is a convenient point to digress a bit on the question of roughness. At first sight, it might appear that the roughness of a surface depends merely on handling. However, turns out that this is not always the case. In crystal growth, it is observed that cooperative effects can considerably influence the surface structure. Below a certain temperature $T_R$, the surface is generally flat with a few aggregation of atoms and a few vacancies within the plane. Above $T_R$, the surface becomes rough.

Figure 4 shows models of crystal surfaces obtained by Monte-Carlo simulation (Muller Krumhhaar 1979). The transition to a rough structure is visible. Referred to as the roughening transition, it has similarities to phase transition.

The roughening of a three-dimensional lattice system is ascribed essentially to fluctuations, the efficacy of the latter being dictated by the energetics involved. Approaching $T_R$ from below, only small wavelength fluctuations are initially favoured. Thus, at first, only small islands and holes are formed, surrounded by steps of finite length. Towards $T_R$, the free energy of such steps decreases and