# Continuum modelling for adhesion between paint surfaces

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## ARTICLE INFO

## ABSTRACT

A mathematical model is proposed to describe the interaction between graphite, polyester and silica solid substrates whose surfaces are functionalized by hydroxyl group, carboxyl group and fluorine atoms. Assuming a relaxed form of these solid substrates, they are modelled as rectangular boxes, while the functional groups are modelled as boundary surfaces. Using the 6–12 Lennard–Jones potential together with a continuum approximation, the total van der Waals interaction energy is obtained as a function of the interfacial separation distance between two surfaces of the solid substrates. Here, the adhesion energy is the minimum energy calculated at the equilibrium separation distance. Our results reveal that among the substrates studied, graphite has the potential to be used as a base material in paints because of its strong adhesion when it is paired with either polyester or silica surfaces.

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## 1. Introduction

Paint colours commonly consist of four components, namely, binders, volatile substances, pigments, and additives [1]. The binders are the backbone of the colour which tie the other parts together. The volatile substances reduce the stickiness of the colour, and when they evaporate thus strengthen the adhesion. The pigments play key roles in displaying the colour as well as intensifying the paint. An example of a pigment is carbonaceous which provides high strength and resistance. Lastly, the additives, also known as extenders, boost the efficiency of the paint, and some of them, such as silica, can protect the finished products from pollutants.

Paint colours have been continuously improved to endure environmental conditions. In particular, the studies in this field focus on two aspects which are to prevent adhesion from contaminants and to increase the adhesion of the paint to a surface. Yarovsky and Evans [2] showed that crosslinked epoxy resin can improve the resistance to soiling of polyester based fabrics. Henry et al. [3] attached some functional groups, namely hydroxyl and carboxyl groups, and fluorine atoms to polyester-based surfaces leading to the reduction of the adhesion between such surfaces and contaminants. Moreover, Yiapanis [4] introduced the self-cleaning properties of a lotus leaf to polyester-based surfaces

which minimise the adhesion of water droplets onto those surfaces.

The properties of paints are generally investigated using either experimental or computational approaches. Well-known computation techniques are atomistic simulations and molecular dynamics studies. In Henry et al. [5], the adhesion between graphite and modified polyester surfaces was studied. They functionalized the surfaces by hydroxyl groups, carboxyl groups, and fluorine atoms and examined the effects of the adhesion with and without the effect of surface relaxation by using the COMPASS force field. In Natarajan et al. [6] the interfacial energy and the adhesion of atactic polypropylene and poly (1,4-cis-butadiene) surfaces was investigated. Wu and Xu [7] investigated the consequences of the crosslinked-epoxy resin. In particular, Henry et al. [5], Natarajan et al. [6], and Wu and Xu [7] used atomistic simulations to study various aspects of paints.

The aim of this paper is to analytically determine the adhesion energy between graphite, polyester, and silica surfaces. Also, the introduction of hydroxyl groups (OH), carboxyl groups (COOH), and fluorine atoms (F) to such surfaces is considered. Instead of adopting discrete atomistic simulation, we use a continuous approach, which is much less computationally expensive. We note that this approach was successfully used to model the interaction between fullerene and a phospholipid bilayer [8] and was also effectively employed to describe the energy behaviours of carbon nanostructures [9,10].

This paper is structured as follows. In the following section, the continuum approach together with the procedures to obtain the adhesion energy is described. In Section 3, numerical results are

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given for the adhesion between various surfaces. Finally, we provide a summary in Section 4.

## 2. Model formation

Adhesion energy is one of the most important properties for paints which indicates the strength of the interaction between any two materials. It can be theoretically characterised by the separation energy, which for the materials studied here depends only on the van der Waals interaction [3]. We employ the $6-12$ Lennard–Jones potential function (1) to model the van der Waals interaction, namely,

$$\Phi = \epsilon \left[ -2\left(\frac{\sigma}{\rho}\right)^6 + \left(\frac{\sigma}{\rho}\right)^{12} \right] = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}}, \qquad (1)$$

where $\rho$ is the distance between any two atoms in the interacting molecules, $\epsilon$ is the energy well depth, $\sigma$ is the van der Waals diameter, $A = 2\epsilon\sigma^6$ and $B = \epsilon\sigma^{12}$ are the attractive and repulsive Lennard–Jones constants, respectively. We note that the attractive and repulsive Lennard–Jones constants are derived from the linear combination of the proportion of the atomic types of the two interacting molecules, where the information for each type of atom is taken from [11]. Moreover, the mixing rules [12] are utilised in the system of two different atomic types, which are $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. For instance, the Lennard–Jones constants of the silica–silica system are obtained as

$$A = \frac{1}{9}A_{\mathrm{Si,Si}} + \frac{4}{9}A_{\mathrm{Si,O}} + \frac{4}{9}A_{\mathrm{O,O}},$$

$$B = \frac{1}{9}B_{\mathrm{Si,Si}} + \frac{4}{9}B_{\mathrm{Si,O}} + \frac{4}{9}B_{\mathrm{O,O}},$$

where $A_{i,j}$ and $B_{i,j}$ signify the interaction between atoms $i$ and $j$. All of the Lennard–Jones constants for the systems studied in this paper are given in Table 1. We comment that the interaction energy here is dominated by the van der Waals energy and we ignore the electrostatic interaction due to the zero point charge on the surfaces in the assumed vacuum environment [13]. As also supported by [14], the van der Waals interaction plays a more important role over the electrostatic energy in vacuum.

Here, the solid substrates are assumed to be in a relaxed form, where their surfaces are flatter compared to an unrelaxed state as to maintain their stability [5]. Based on the structure of the materials shown in [3,5], we model the solid substrates as rectangular boxes and the functional groups as flat planes lying on top of the rectangular boxes. To facilitate the derivation of the exact form for the interaction energy, we adopt a continuum approach where we assume the uniform distribution of atoms within the volume of the rectangular boxes. Similarly, we assume the uniform atomic distribution on the surface of the flat planes.

We comment that the continuous model adopted here gives results that may be closer to reality than a discrete set of Lennard–Jones centres which is obtained from the sum of the interactions (1) for each atom pair [15].

From the above assumptions, the total energy of the system can be written as

$$E = \eta_1 \eta_2 \int_{X_1} \int_{X_2} \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) dX_2 \, dX_1, \qquad (2)$$

where, depending on the interacting structures, $\eta_i$ $(i = 1, 2)$ can be either the mean atomic volume densities or the mean atomic surface densities of the two molecules, and $dX_i$ $(i = 1, 2)$ can denote either the surfaces or the volumes of the elements.

The mean atomic volume densities and mean atomic surface densities for the materials studied here are adopted from the atomistic simulations [3,5] and are given in Table 2. For the modified surfaces, the mean atomic densities refer to the densities of the functional groups per unit area of the surfaces. We comment that the number in front of the additional function groups represents the number of substituents per unit cell surface area, for example there are seven hydroxyl substituents per unit cell, hence Polyester7OH.

We comment that in [3,5] the van der Waals interaction energy, between surfaces in vacuum, is described using the Hamaker equation, which is based on Hamaker [16] and Israelachvili [17]. The Hamaker equation as shown in [17] and used in [3,5] is given by

$$W(d) = -\frac{A_{12}}{12\pi d^2},$$

where $d$ is the interfacial separation and $A_{12}$ is the Hamaker constant, which is proportional to the properties of the materials involved and is given by

$$A_{12} = \pi^2 C_{12}\rho_1\rho_2,$$

where $\rho_1$ and $\rho_2$ are the atoms per unit volume in surfaces 1 and 2, respectively, and $C_{12}$ is the coefficient in the atom–atom pair potential which reflects the chemical composition of the surfaces. We note that there are similarities in the continuum approximation of the Lennard–Jones potential given in (2) and the above Hamaker equation, where both are dependent on the composition of atoms making up the surfaces and the atomic densities of the surfaces. As shown in Section 3, the van der Waals interaction energy obtained from both methods are in good agreement. However, we emphasise our major contribution here which is the

**Table 1**
Lennard–Jones constants used in the model.

| Material | $A$ (kcal mol$^{-1}$Å$^6$) | $B$ (kcal mol$^{-1}$Å$^{12}$) |
|---|---|---|
| Graphite–Graphite | $6.675 \times 10^2$ | $1.171 \times 10^6$ |
| Polyester–Polyester | $2.278 \times 10^2$ | $3.094 \times 10^5$ |
| Silica–Silica | $1.039 \times 10^3$ | $2.149 \times 10^6$ |
| Graphite–Polyester | $3.909 \times 10^2$ | $6.031 \times 10^5$ |
| Graphite–Silica | $8.327 \times 10^2$ | $1.590 \times 10^6$ |
| Polyester–Silica | $4.880 \times 10^2$ | $8.224 \times 10^5$ |
| Graphite–OH | $3.018 \times 10^2$ | $3.433 \times 10^5$ |
| Graphite–COOH | $4.308 \times 10^2$ | $5.985 \times 10^5$ |
| Graphite–F | $4.159 \times 10^2$ | $5.209 \times 10^5$ |
| Polyester–OH | $1.745 \times 10^2$ | $1.741 \times 10^5$ |

**Table 2**
Mean atomic volume densities and mean atomic surface densities for the surfaces [3,5].

| Material | Mean atomic density |
|---|---|
| Graphite | $1.261 \times 10^{-1}$ per Å$^3$ |
| Polyester | $8.760 \times 10^{-2}$ per Å$^3$ |
| Silica | $5.600 \times 10^{-2}$ per Å$^3$ |
| Polyester7OH | $4.375 \times 10^{-3}$ per Å$^2$ |
| Polyester15OH | $9.375 \times 10^{-3}$ per Å$^2$ |
| Polyester7COOH | $4.375 \times 10^{-3}$ per Å$^2$ |
| Polyester15COOH | $9.375 \times 10^{-3}$ per Å$^2$ |
| Polyester7F | $4.375 \times 10^{-3}$ per Å$^2$ |
| Polyester15F | $9.375 \times 10^{-3}$ per Å$^2$ |
| Silica23OH | $1.438 \times 10^{-2}$ per Å$^2$ |
| Silica35OH | $2.188 \times 10^{-2}$ per Å$^2$ |
| Silica58OH | $3.625 \times 10^{-3}$ per Å$^2$ |