Molecular Dynamics modelling of the adhesive interaction between fine particles

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In this work we propose a Molecular Dynamics method to model the frictionless adhesive interaction force between two fine cohesive polymer grains. The model consists of three main steps: firstly, we build a simple model of the bulk material for these grains, using only two microscopic internal parameters (the bond energy and the equilibrium distance between atoms in an amorphous lattice). To have big enough specimens, an inhomogeneous distribution of the atoms size prepared in layers has been implemented. Atoms with minimum size belong to the area of contact, giving in this manner a higher resolution near the contact area. Secondly, the cohesion strength (i.e., the work of adhesion) is derived from the interaction potential of the atoms of the grain with the wall. Finally, we simplify the computational problem, solving the equivalent contact problem of sphere-plane interaction. The contact zone is essentially given by the asperity size, therefore the adhesion between the asperity and the plane is calculated as a sum of interactions between atoms of the asperity and the plane. A computational experiment of pull-on is carried out to study the influence of the adhesion on the formation of the contact area and forces between two polymer-based toner particles of 10 microns with asperities of the order of 0.2 micron. Finally, the numerical results are compared with theoretical predictions, and a good agreement is observed.

1 INTRODUCTION

There is no a general model of the contact mechanic between two bodies. Several approximations, both theoretical and numerical, have been carried out to solve particular cases. Hertz (Hertz 1882) in year 1880, solved theoretically the problem of two cohesionless elastic spheres at contact under an external quasi-static load. Scientists have used this model as a base to develop new theories to give answers to problems related to the contact. The adhesive contact is of great importance because cohesive powders are used in various industrial sectors (like medical, pharmaceutical, xerographic, etc.). Cohesive materials raise a wide variety of unsolved problems, involving the grains nature (shape, weight, size, etc.) and the mechanical situation under which they can be found (flow, compression, shaking, etc.). Thus, an important effort has focused on the problem of the adhesive contact among an ensemble of bodies. This is a very complex problem and the success of the analysis (theoretical, experimental or numerical) rests on the exactitude of the used contact model. Theories for the elastic contact have been developed, such as the DMT model proposed by Derjaguin, Muller and Toporov (B. V. Derjaguin & Toporov 1975) or the JKR model by Johnson, Kendall and Roberts (K. L. Johnson & Roberts 1971). These are two important limits in the problem of the adhesive *elastic* contact, since the first one implicitly assumes a relatively weak adhesive elastic contact between two small spherical hard solids, and the second is considering a stronger adhesive contact between two large softer spherical bodies. The Tabor's parameter (Tabor 1977) governs when of these theories can be applied. Many other authors have contributed with interesting works such as Greenwood and Johnson (Greenwood & Johnson 1998) who formulated a analytical model providing a good approach of the adhesive force.

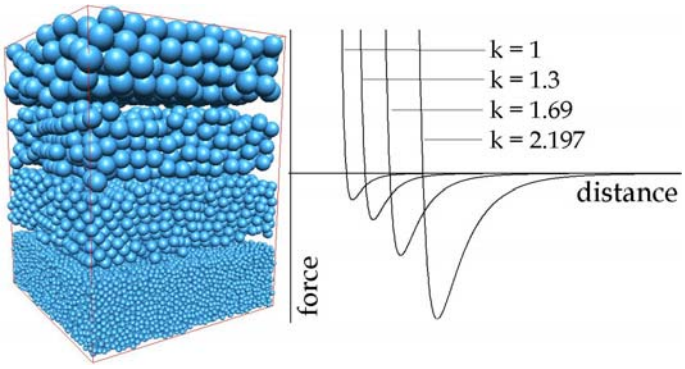

Figure 1. Detail of the building in layers .

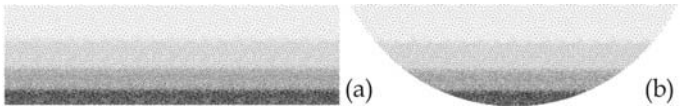

Figure 2. Sample of the computer bulk material with 4 layers, (a) block to be used in compression tests and (b) spherical surface to be used in the contact adhesive zone.

This work reports a numerical model of the adhesive and non-adhesive contact using direct Molecular Dynamic simulation. In section 2 a computer bulk material with well-defined mechanical properties such as Young's modulus and Poisson's coefficient is designed. Section 3 describes the microscopic model of adhesive interaction between two surfaces. A numerical realization of the pull-on and pull-off experiment is exposed in section 4, showing the results obtained with and without adhesion. Theoretical models are used to validate the mechanical contact of our proposed numerical model.

2 COMPUTER BULK MATERIAL

The bulk material is generated using an aggregate of spheres which are joined by the action of a fitness empirical potential. These spheres are the basic units of the computer bulk material. Depending on the degree of accuracy in the description of the material, one finds two levels: for large bodies ($\sim mm$) a mesoscopic scale level can be accepted, where these elemental units are representative points of the material. However, for bodies small enough ($\sim \mu m$), the number of these units can be the same as the number of real atoms, in which case we will refer to these units as atoms, and our description is truly microscopic. In this paper we will work inside the second description since our interest is focused on the contact between micro-sized powder particles. Using Molecular Dynamics approach, this material is represented as an amorphous ensemble of atoms interacting via the Lennard-Jones potential. Parameters of this potential, D (the bond energy) and a (the equilibrium distance) are linked with macroscopic mechanical magnitude such as Young's modulus E according to $E = \lambda D/a^3$, where λ is a rational number which depends on the type of the structure and the interaction range. Through uniaxial compression tests, D and a are empirically adjusted in such a way that mechanical properties of the computer bulk material are close to the real bulk material used to manufacture the fine particles (for example, polystyrene). We considered $T = 10^{-3}D/K_B = 0.3$ K (T is the temperature and K_B the Boltzmann's constant) as the contact problem is non-thermal. Using this condition of low temperature, the computational tests of compression provide the closest values of the theoretical elastic moduli. The computational technique involved in this process to adjust these parameters can be found in (Gilabert et al. 2002). In the present work we introduce a novelty in the design of this material. The idea consists of creating a block of this bulk material but arranged by layers, as shown figure 1, where we can see a detailed view of the process of layering. Once layers have been joined and the equilibrium is attained ,the material is ready (figure 2a). Each layer has a different atom size. When we say "atom size" we actually mean *equilibrium distances* inside the amorphous lattice. Relation between the size of atoms belonging to a couple of adjacent layers scales as $a_{l+1} = k\ a_l$ ($l \geq 0$), where a_{l+1} is the atom size for the layer $l+1$ and a_l for the layer l. The first layer of atoms contains the smallest atom size and we denote this size as a, and its value is equal to 4 $\mathring{A}$. Thus, size atom from the $n\ th$ layer is $a_n = k^n\ a$. Taking into account this condition, the potential energy between atoms from two contiguous layers l and m is

$$\Pi(r_{ij}) = D_{lm}\left[\left(\frac{a_{lm}}{r_{ij}}\right)^{12} - 2\left(\frac{a_{lm}}{r_{ij}}\right)^{6}\right]. \quad (1)$$

where r_{ij} is the distance between atoms. With this arrangement The elastic moduli are invariant if the potential parameters satisfy the following scaling formulae

$$a_{lm} = \gamma_{lm}\ a \qquad D_{lm} = \gamma_{lm}^3\ D \qquad \gamma_{lm} = \frac{k^l + k^m}{2}. \quad (2)$$

To check that this scaling is correct, we have performed tests of compression to measure Young's modulus E, Poisson's coefficient ν and the bulk modulus K. A wide variety of specimens have been created, varying the number of atoms (n), the number of layers (n_l) and the scaling size factor (k). Table 1 shows the results of some mechanical tests for these layered materials. Note that the case $n_l = 1$ is the homogeneous material. The unit for the stress is $\sigma_0 \stackrel{\text{def}}{=} f_{\max}/a^2$, where $f_{\max}$ is the necessary strength

Table 1. Elastic moduli computed for different configurations of the computer bulk layered material.

n_l	k	n	E/σ_0	ν	K/σ_0
1	1.0	8000	22.5 ± 0.8	0.377 ± 0.004	31.05 ± 0.07
2	1.3	4737	22.48 ± 0.02	0.380 ± 0.002	32.4 ± 0.4
2	1.4	1626	22.55 ± 0.07	0.379 ± 0.001	31.8 ± 0.3
2	1.5	5113	23.105 ± 0.014	0.3765 ± 0.0002	31.32 ± 0.06
3	1.3	7924	23.5 ± 0.1	0.375 ± 0.001	31.78 ± 0.12
4	1.3	8728	23.0 ± 0.4	0.379 ± 0.003	31.9 ± 0.2

to break the bond between two atoms belonging to $l = 1$. We denote the unit for the material density as ρ_0. For all computer materials, the average density was $\rho/\rho_0 = 1.009 \pm 0.001$. Choosing $\sigma_0 = 160$ MPa together with $\rho_0 = 1056$ kg/m^3 gives properties similar to real polymers material, $E \simeq 3.6$ GPa, $\nu \simeq 0.38$, $K \simeq 50$ GPa and $\rho \simeq 1065$ Kg/m^3 (Fried 1995).

The next step is cut this block in such a way that a spherical surface (with reduced radius of curvature R^*) is obtained (see figure 2b). After the cut, the surface needs time to reach the mechanical and thermal equilibrium. The atoms in the upper side of this polar cup are clamped in their equilibrium positions. It is assumed that the model is thick enough so that deformations initiated in the contact zone die away before they reach the clamped atoms. Justification for designing this heterogeneous material is based on two reasons: first, the number of atoms needed to perform the model is drastically reduced (between $60\% - 80\%$, depending on n_l and k), and second, this layering allows to increase the resolution (i.e., the numerical density of atoms) at the area of contact (corresponding to index layer $l = 1$).

3 MODELLING ADHESIVE INTERACTION

For the powder particles the effective area of contact is given by the contact between small asperities (Massimilla & Donsi 1976; T. Mason & Halsey 2000). Therefore, we use this spherical surface as a numerical model of an asperity with a typical radius $R_{asp} \sim 0.1\ \mu$m. We propose to perform the contact realization between a couple of asperities introducing a simplification: the equivalent contact problem of the sphere-plane interaction (Johnson 1985). To model the adhesive interaction between the asperity and the rigid plane, the analytical expression given by

$$U(z) = \int_V \Pi(r)\, \rho_n\, dV \tag{3}$$

for the interaction energy between a single atom from the first layer of the asperity and the plane has been used. In this expression, ρ_n is the numerical density (number atoms per unit volume) in the plane and z is distance atom-plane. The integral is extended to the half-space volume occupied by the rigid plane. Atoms belonging to layers with $l > 1$ do not contribute to the adhesive energy since they are out of the range interaction. The work of adhesion w (the specific energy needed to separate two surfaces in contact) can be obtained as follows: 1) obtain the potential energy, $W(z)$, between two half-spaces integrating the expression 3 (Israelachvili 1991); 2) calculate the equilibrium distance from $|W'(z)|_{z=z_{eq}} = 0$; and 3) substitute this equilibrium distance in $W(z)$. In this way, the work of adhesion w is

$$w = \sqrt[3]{\frac{15\,\pi^3}{512}}\, \rho_n^{(1)}\, \rho_n^{(2)}\, D_{12}\, a^4 \tag{4}$$

where $\rho_n^{(1)}$ and $\rho_n^{(2)}$ are the numerical density of atoms on adhesive surfaces named as 1 and 2 respectively separated by $z_{eq} = a/\sqrt[6]{15}$. D_{12} is the bond energy between two atoms from surfaces 1 and 2 resp.

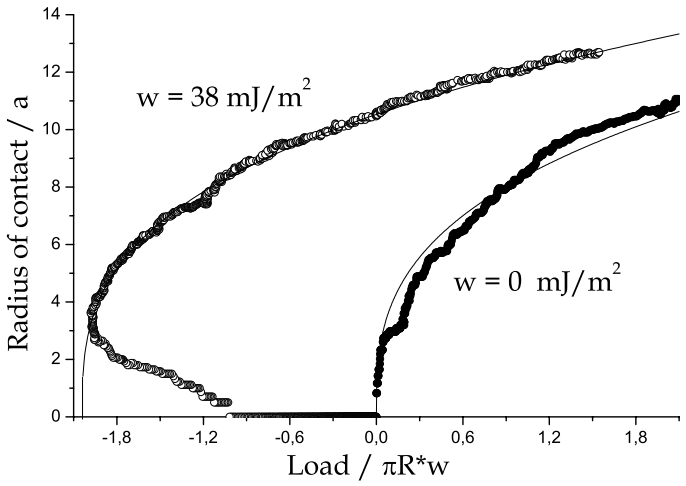

Figure 3. Symbols: numerical results of the non-adhesive ($w = 0$) and adhesive ($w \neq 0$) contact. Lines: theoretical prediction provided by Hertz and DMT models.

4 NUMERICAL EXPERIMENT OF THE ADHESIVE AND NON-ADHESIVE CONTACT

The force necessary to separate two adhesive particles can be obtained from the so-called pull-on/pull-off experiments. We simulate numerically this experiment to observe the behavior of our numerical model. To produce the necessary load and deformation on the model of asperity, the rigid plane is moved with a preset velocity. This velocity of deformation is low enough to consider the process as quasi-static. To measure the area of contact, we assume that each atom at a distance $z = \sqrt[6]{5}a$ (the equilibrium distance of the potential 3) from the plane contributes with an effective cross-section given by πz^2.

In this work we report the results obtained for two cases. The first case is for cohesionless contact. To reproduce the non-adhesive contact we have taken into account a very low value of the bond energy D_{12} in 4. Concretely $D_{12}/D \simeq 10^{-6}$ is small enough to obtain $w \approx 0$. This case would correspond with the Hertzian model of cohesionless contact. For the second case we take $w = 38$ mJ/m^2 since this is a classical value

for polystyrene (the typical values of w for polymers are within the interval $0.01 - 0.07$ J/m^2 (Ross & Morrison 1988)). For our model, the magnitude D_{12} modulates the strength of the adhesion. We show in figure 3 the results of the simulation for both cases. To compare the obtained adhesive behavior with theoretical models, we just calculate the Tabor's parameter (Tabor 1977)

$$\mu = \left(\frac{R^* w^2}{z_0^3 (E^*)^2} \right)^{\frac{1}{3}} \tag{5}$$

which is the ratio between the amplitude of the elastic deformation when the contact is broken and the range of interaction of the adhesive forces. E^* is the reduced Young's modulus and the distance z_0 is the minimum possible distance between the adhesive surfaces. The computed value for the current simulations was $z_0 = 0.6498a$, which is very close to the theoretical value of $z_{eq} = a/\sqrt[6]{15} \simeq 0.6368a$ used to derive the formula 4. For this numerical experiment $\mu = 0.7$. In the literature it is accepted that the DMT model ($F = -2\pi R^* w$) is applicable when $\mu < 0.1$, while for $\mu > 5$ the JKR ($F = -3/2\pi R^* w$) model is more appropriate. Thus we compare our results with DMT prediction. The force computed from the present numerical experiment was $F = -1.896\pi R^* w$. Therefore a good agreement (difference about 5%) with this value of the force can be observed. One must be taken into account that our case are in the middle of the DMT-JKR interval, although closer to DMT, which could explain this slight disagreement. In figure 3, the Hertz and DMT predictions (straight lines) are represented together with the simulated results.

5 CONCLUSIONS

A simple but efficient model of the bulk material specially designed to reproduce well-defined mechanical properties has been developed using using Molecular Dynamics. By means of this technique, a microscopical model of adhesion between elemental constituents (atoms) has been proposed. The adhesive and non-adhesive contact problem between asperities has been simulated using the equivalent contact sphere-plane problem. A good agreement with the elastic contact theories has been obtained.

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