

# Advancing the self-healing properties of polymer-coated surfaces by applying thrombosis-inspired modeling

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**ABSTRACT:** The paper shows a sample application of an innovative modeling technique (Dissipative Particle Dynamics – DPD) as a possible tool for multi-scale modeling of the behavior of the advanced engineering materials (e.g. coated materials and/or multi-materials). The multi-scale modeling of the behavior of the advanced engineering materials is related primarily to development of new techniques and methods needed to bridge the gap between the atomistic scale and macro applications. The presented example of examining applicability of the DPD to damage assessment, dealing with the problem of interaction of particles, polymers and surfaces, is an issue concerning many applications in colloid science. It has confirmed the applicability of DPD as method for linking the macro and atomistic scales. The imminent application of the method and the example are in the area of “self-healing” advanced engineering materials, thus in line with the objectives of NiSIS.

**KEYWORDS:** DPD, Self-healing, nature-inspired, polymer-coated

## INTRODUCTION

Polymer coatings, otherwise extremely suitable engineering for coating of, e.g. steel in chemistry medicine and other areas, can be very tedious and expensive, if not impossible to repair if damaged, due to i.e. need to repair the whole surface, need to shut-down the installation, need to bring in completely different (very specialized) maintenance teams. As a solution, a modeling inspired on thrombosis phenomena combined with neuron model can be introduced in order to improve the properties of the polymer coatings by applying/developing an “intelligent self-healing material for industrial (electronics) applications”.

## THE DPD METHOD

### GENERAL BACKGROUND

Many practical issues in colloid science concern the interaction of particles, polymers, and surfaces. The technique of dissipative particle dynamics (DPD) has been initially implemented to the problems of controlling the effects of soot and deposition (e.g. in diesel engine lubricants or surface fouling in chemical reactors) but it is also a suitable alternative technique for simulating the hydrodynamic behavior of other colloid–polymer–solvent systems. Hoogerbrugge and Koelman (1992) have suggested a new Dissipative Particle Dynamics (DPD) approach to simulate flow fields of incompressible complex fluids. The fluid is divided into mesoscale particles so that each particle contains a large number of molecules but is still much smaller than the dimensions of the containing vessel. Based on concepts prevalent in molecular dynamics (MD) theory a Langevin equation was postulated by which the motion of the fluid particles can be calculated. The forces exerted on every particle by its neighbors, that are within a prescribed distance  $r_c$  (radius of influence) from it, are normally divided into three categories; conservative repulsive forces that can be derived from a potential function, dissipative forces that stem from viscous friction generated by the relative translational motion of adjacent particles, and random forces that may be significant due to the mesoscale dimension of the particles.

One of the controversial, unsettled aspects in DPD modelling relates to the formulation of the proper no-slip conditions near a rigid wall. The Lees-Edwards method (Lees and Edwards, 1972) in essence, circumvented the problem of how to

avoid particles that can both penetrate and slide along rigid walls. Their ingenious suggestion that worked quite well for Couette flows, in which particles penetrating one wall should be reintroduced at the other wall, can hardly be qualified as a condition that should be applied locally at any rigid wall in more complex flow systems. A more advanced suggestion was to freeze regions of fluid near the rigid wall (Hoogerbrugge and Koelman, 1992; Boek et al., 1996). This, however, resulted in possible particle penetration through the walls due to the ‘soft’ conservative potential (Revenga et al., 1998). To avoid such non-physical results various methods have been suggested that combine the freezing particle layer near the wall with specular, bounce-back or Maxwellian reflection of a particle reaching a rigid wall (e.g., Hoogerbrugge and Koelman, 1992; Revenga et al., 1998). More recently, Pivkin and Karniadakis (to be published) suggested combining the above with an augmented conservative force at the rigid wall. Flekkoy and Coveney (1999) and in particular Flekkoy et al. (2000) have suggested to link the DPD and Molecular Dynamics (MD) equations that govern the motion of the mesoscopic and molecular size particles, respectively (a bottom-up strategy). However, to reach closure it was still required to define constitutive relations prevailing at the continuum level (top-down strategy). Thus, the friction coefficient was linked to the dynamic viscosity of a Newtonian fluid perceived as a continuum and the ratio between intersection length and distance between two interacting Voronoi cells. In this article, we adopt the strategy initiated by Hoogerbrugge and Koelman (1992) and further developed by Espanol and Warren (1995) and Espanol (1998), namely, that the DPD equations governing the motion of identical, mesoscopic particles, are postulated.

### DPD EQUATIONS OF MOTION

During more than a decade, a considerable number of articles have focused on the proper formulation for the constitutive equations governing the different forces, and how their a-priori unknown parameters are related to the known phenomenological coefficients of the fluid. A widely accepted formulation for the equations of motion of a DPD particle is (e.g. Espanol and Warren (1995), Groot and Warren (1997), Novik and Coveney (1997), Besold et al. (2000), Pivkin and Karniadakis, to be published)

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt \\ d\mathbf{v}_i &= \sum_{j \neq i} \mathbf{F}_{ij} dt = \sum_{j \neq i} (\mathbf{F}_{ij}^C dt + \mathbf{F}_{ij}^D dt + \mathbf{F}_{ij}^R dt^{1/2}) \end{aligned} \quad (1)$$

where  $d\mathbf{r}_i$  and  $d\mathbf{v}_i$  are the infinitesimal displacement and velocity change, measured relative to a Galilean coordinate system, that particle  $i$  undergoes during the time increment  $dt$ . The forces  $\mathbf{F}_{ij}^C$ ,  $\mathbf{F}_{ij}^D$  and  $\mathbf{F}_{ij}^R$  are the conservative (repulsive), dissipative and random forces (per unit mass of particle  $i$ ) that particle  $j$  exerts on particle  $i$ , respectively, provided particle  $j$  is within the radius of influence  $r_c$  of particle  $i$ :

$$\begin{aligned} \mathbf{F}_{ij}^C &= a_{ij} (1 - r_{ij} / r_c) \mathbf{e}_{ij} \\ \mathbf{F}_{ij}^D &= -\gamma (1 - r_{ij} / r_c)^2 (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}) \mathbf{e}_{ij} \\ \mathbf{F}_{ij}^R &= (2k_B T \gamma / m_i)^{1/2} (1 - r_{ij} / r_c) \xi_{ij} \mathbf{e}_{ij} \end{aligned} \quad (2)$$

Here,  $a_{ij}$  is the maximum repulsion force per unit mass,  $r_{ij}$  is the distance between particles  $i$  and  $j$ ,  $\mathbf{e}_{ij}$  is a unit vector pointing in a direction from  $j$  to  $i$ ,  $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$  is the velocity of particle  $i$  relative to that of particle  $j$ ,  $m_i$  is the mass of particle  $i$ ,  $\gamma$  stands for the friction coefficient,  $k_B$  is the Boltzmann constant,  $T$  is the equilibrium temperature and  $\xi_{ij}$  is a random number with zero mean and unit variance. In case  $r_{ij} > r_c$  particle  $j$  is assumed to exert no force on particle  $i$ . Notice that the conservative, dissipative and random forces that particle  $j$  exerts on particle  $i$  were assumed to depend upon the distance between these particles, the dissipative force also depends upon a single component of the relative velocity between the particles ( $\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}$ ), and that the direction of all the foregoing forces is along the line connecting the centres of the two particles.

If we define the following dimensionless variables,

$$\begin{aligned} \hat{\mathbf{r}}_i &= \mathbf{r}_i / r_c \\ \hat{r}_{ij} &= r_{ij} / r_c \\ \hat{\mathbf{v}}_{ij} &= \mathbf{v}_{ij} / v_T \\ \hat{t} &= t v_T / r_c \end{aligned} \quad (3)$$

where  $v_T = (k_B T / m_i)^{1/2}$  is the thermal velocity of particle  $i$ , equation (1) can thus be expressed in the following dimensionless form,

$$d\hat{\mathbf{x}}_i = \hat{\mathbf{v}}_i d\hat{t}$$

$$d\hat{\mathbf{v}}_i = \sum_{j \neq i} \frac{a_{ij} r_c}{v_T^2} (1 - \hat{r}_{ij}) \mathbf{e}_{ij} d\hat{t} - \frac{\gamma r_c}{v_T} (1 - \hat{r}_{ij})^2 (\hat{\mathbf{v}}_{ij} \cdot \mathbf{e}_{ij}) \mathbf{e}_{ij} d\hat{t} + \left( \frac{2\gamma r_c}{v_T} \right)^{1/2} (1 - \hat{r}_{ij}) \xi_{ij} \mathbf{e}_{ij} d\hat{t}^{1/2} \quad (4)$$

In case all particles have identical mass and all the  $a_{ij}$  coefficients are equal, eq. (4) depends only on two dimensionless numbers,

$$\hat{a} = a_{ij} r_c / v_T^2; \quad \hat{\gamma} = \gamma r_c / v_T \quad (5)$$

Thus, there is no need to assume that the mass of a particle  $m$ ,  $k_B T$  and  $r_c$  are all unity, an assumption made in many previous studies. It is sufficient to assume that  $v_T$  and  $r_c$  are equal to one and vary  $\gamma$  and  $a_{ij}$  to obtain different DPD fluids. This would be equivalent to setting numerical values to the dimensionless variables  $\hat{a}$  and  $\hat{\gamma}$ .

The boundary conditions would introduce at least two additional dimensionless parameters,

$$\hat{L} = L / r_c; \quad \hat{V}_w = V_w / v_T \quad (6)$$

where  $L$  and  $V_w$  scale the macroscopic size of the system and the velocity of its wall, respectively.

More recently, Espanol (1998) suggested that additional components to the dissipative and the concomitant random forces be added. These included force components perpendicular to  $\mathbf{e}_{ij}$  and the effect of particle rotation. The former is a natural extension based on simple tensorial considerations and the latter stems from the finiteness of the particles. Based on MD theory Flekkoy and Coveney (1999) and Flekkoy et al. (2000) have also obtained that at the DPD mesoscale forces that are not collinear with  $\mathbf{e}_{ij}$  exist. These modifications, however, have not thoroughly been tested and their contribution to the solution accuracy is awaiting further exploration.

## THE DPD SIMULATION MODEL

The simulations are conducted in a three-dimensional simulation box, as shown in Figure 1. A wall of frozen particles is created at one end providing the surface. Although the surface of the wall is square, the periodic boundary conditions make it appear infinite. Polymers are then attached, effectively “chemically grafted,” to this wall. A rough spherical object is created at a given distance from the wall to simulate a colloidal particle. The box is filled with DPD particles which represent the solvent. The wall is divided into two along a plane parallel to the wall–fluid interface. The half to which the polymers are attached is made up of particles identical to those which make up the colloidal particle, while the other half is made up of solvent particles. These solvent particles ensure that the colloidal particle can only reach the wall, and hence adsorb onto its surface, by traveling through the layer of polymers. Another type of structure is the polymer (see Figure 2). Here, a bead-and-spring type model is used to provide an additional force between adjacent particles in the chain. A Fraenkel spring is mainly used:

$$\mathbf{F}_{ij}^p = k(r_{ij} - r_{eq}) \hat{\mathbf{e}}_{ij} \quad (7)$$

where  $k$  is the spring constant and  $r_{eq}$  is the equilibrium spring length.

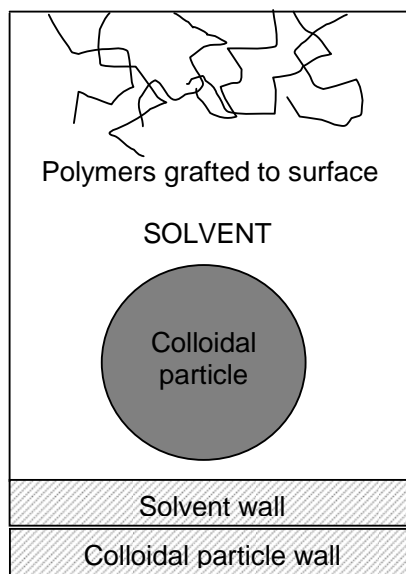


Figure 1 DPD model for adsorption of colloidal particles

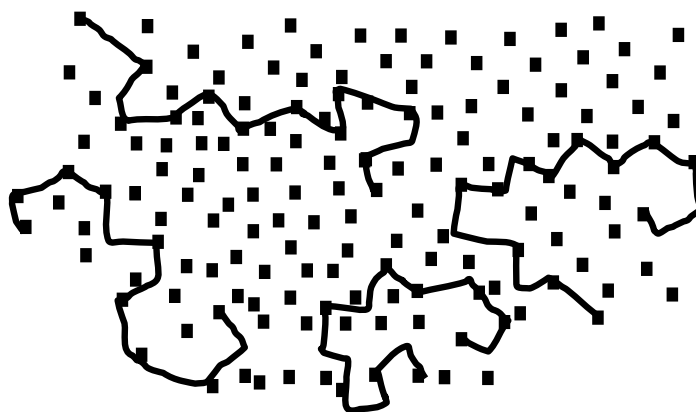


Figure 2 Example of polymer chains

## RESULTS

Adsorption has been defined with the spring constant  $k = 50\text{N/m}$ . The snapshot with distribution of the colloidal particles and solvent particles after  $0.1\text{ s}$  is presented in the Figure 3. Red dots represent colloidal Voronoi elements, blue dots represent solvent Voronoi elements. Our results closely matched those experimentally and numerically recorded by Gibson et al (1998) as it is shown in Figure 4.

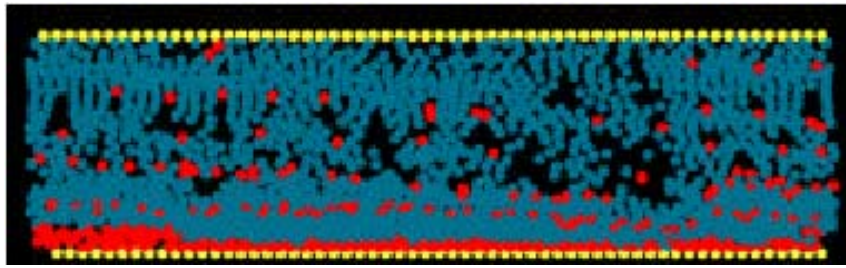


Figure 3 Snapshot after 0.1 s of colloidal particle adsorption

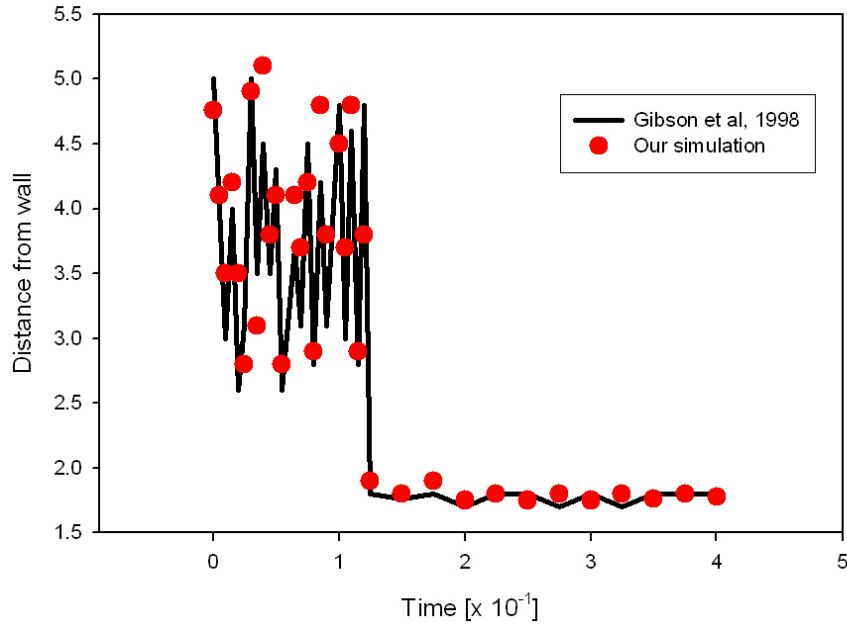


Figure 4 Comparison of results for the colloidal particle adsorption

## DISCUSSION AND CONCLUSIONS

Simulation and modeling of material behavior and degradation mechanisms, dependence of material structure on manufacturing methods and manufacturing processes, is prerequisite for materials and manufacturing method design as well as for the life cycle performance evaluation. The simulations example presented here shows that DPD model is potentially a very useful tool for simulation of the process adsorption on the coated surfaces.

The imminent application of the method and the example are in the area of “self-healing” advanced engineering materials. The method presented in the paper allows doing it up to the point of calculating the probability of deposition as the function of the system looking at the interaction of particles, polymers and surfaces. In that sense, the DPD modelling can be used for the non-invasive repair of damaged coatings (Figure 5).

A significant step and the desirable direction of further work in the area of DPD-based damage modeling and analysis would be the research of “intelligent repair materials” (Jovanovic and Jovanovic, 2006). The corresponding theoretical considerations are already available (Zomaya, 2006) and when combined with the available modeling techniques (Figure 6) could significantly improve current practice in terms of (a) costs, (b) reduced total effort of repair action and (c) significantly less intrusive character of repair, which can be decisive for certain types of application.

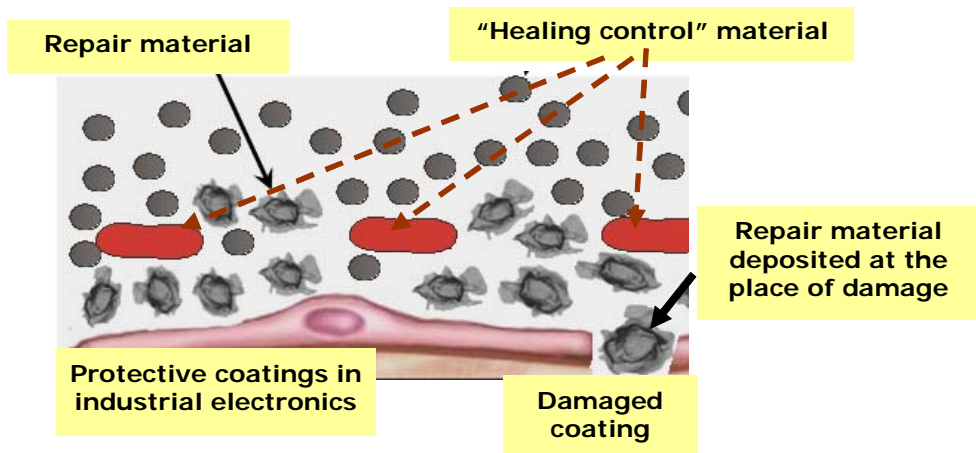


Figure 5 Deposition of the repair material at the damaged coating

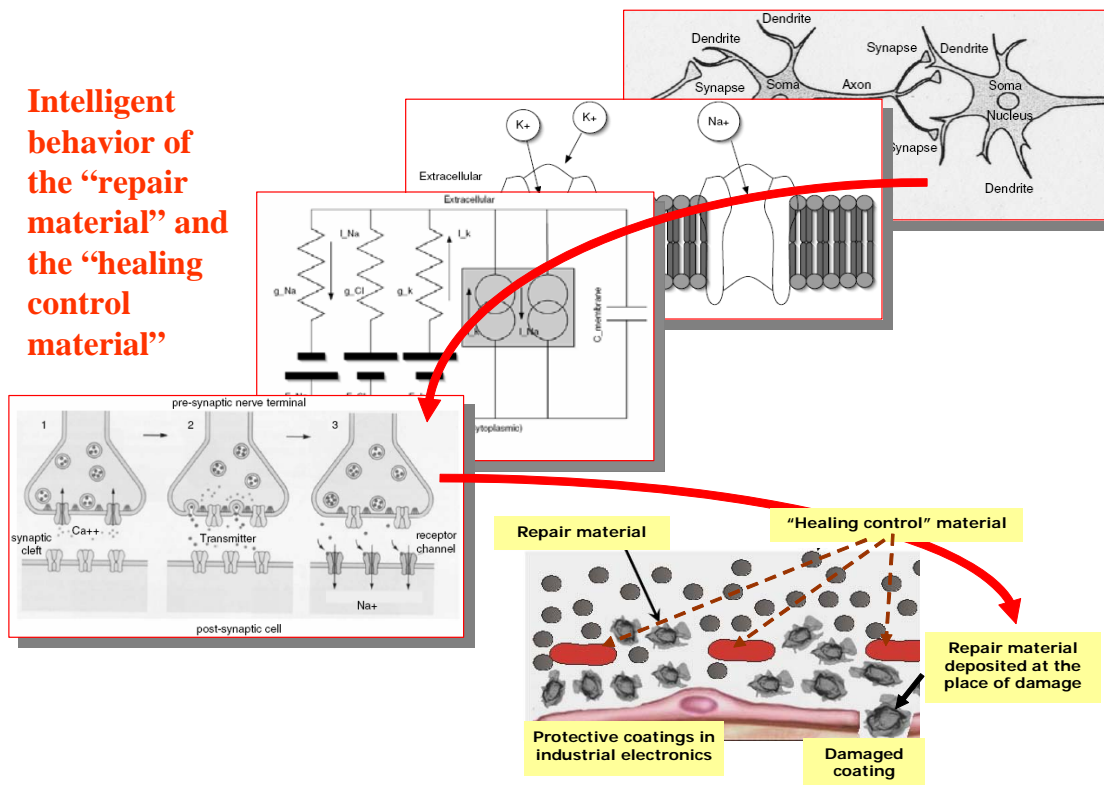


Figure 6 Practical steps in development of intelligent repair materials (from Jovanovic and Jovanovic, 2006; Zomaya, 2006)

The ideal situation would be simulation of the total life cycle. This requires the combination of several research activities which are separated today. For many engineering materials the correlation of microstructure to technical properties e.g. creep is known. However the modelling of the manufacturing process to achieve the optimum microstructure is in infancy. Engineering uses materials data to predict the lifetime of components. However because of not existing correlation of microstructure and materials data safety factors are included which will not exploit the engineering materials potential. Therefore the vision is to develop a virtual manufacturing chain with optimized materials technology and low scatter output.

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