

OFF-CENTER COLLISIONAL MODEL OF PATCHY COLLOIDS

AGNIESZKA CHRZANOWSKA[†], PAWEŁ KARBOWNICZEK, JAN KURZYK

Institute of Physics, Tadeusz Kościuszko Cracow University of Technology
Podchorążych 1, 30-084 Kraków, Poland

*(Received May 29, 2015; revised version received August 4, 2015;
final version received August 19, 2015)*

Momentum transfer resulting from the interaction of two patches on the colloidal particle surfaces is, by nature, off-center and is responsible for particle's rotations. We present how to compute exchange of momentum and angular momentum in the case when patches interact via a square well potential. Elements of the presented algorithm consist mostly of physical and geometrical conditions, partly requiring numerical calculations. The model has been applied to the two-dimensional system of spherical particles with three patches equally placed on the edge of the particles. An example of typical collisional frequencies resulting from molecular dynamics applied to a Monte Carlo equilibrated configuration and its comparison to the case with an unbonded hexagonal starting configuration have been given. It has been shown that at the agglomerated state, when particles are positionally arrested, the dynamics is dominated by the bounces with the borders of the potential well without hitting the cores of the particles.

DOI:10.5506/APhysPolB.46.2535

PACS numbers: 61.20.Ja, 82.70.Dd

1. Introduction

Attention attracted by colloidal particles commensurates with the progress in fabrication of the well-defined objects with dimensions ranging from nanometers to micrometers. The main asset of the colloids lies in the fact that the interactions between colloidal particles may be controlled, thus allowing for realization of new scenarios of structural and thermodynamic behavior [1–5]. Recently, the so-called patchy colloids have become a subject of intense research. The surfaces of such particles are decorated with interacting spots that can attract each other and form bonds (discrete bonding

[†] Corresponding author: achrzano@usk.pk.edu.pl

sites). Their number, size and strength can be tunable. As a result of the bonds, they may organize into structures for functional materials and devices. A promising approach is the self-assembly, which is the spontaneous organization of matter into ordered structures. On the theoretical side, studies based on the theory of associating fluids [6–11] and computer simulations of simple models have provided a great number of new results [12–15]. Theoretical efforts help also in studying new phenomena such as condensation and clustering *e.g.*, present in protein solutions or strongly dipolar fluids [16]. In industrial contexts [17], a model of hard particles with patches has been successfully used to describe behavior of pure or mixed chain molecules. Another challenge is to provide a route to designing ideal gels [18] or successful control of a wide range of equilibrium self-assembled structures.

Dynamical properties of patchy colloids form another class of problems. First of all, it requires noting that during a collision, regardless of the form of the patch–patch interaction used, the transfer of momentum is not along the center–center line, but at the patch–patch line. Although there exist models describing anisotropic particle rotations based on the center–center direction (*e.g.* the Gay–Berne or Ruygrok potential in liquid crystals), the off-center interactions are neither worked out nor popular in molecular dynamics study, most likely due to its complexity. In the present paper, we show how to compute the exchange of momentum and angular momentum in the case when the patches interact via the square well potential for the purpose of the event driven molecular dynamics and the resulting outcome of the event driven simulations. The proposed algorithm is built from the blocks that are mainly conditions of physical or geometrical nature but it also requires numerical work based on the small time steps like in the standard molecular dynamics.

The paper is organized as follows. Section 2 describes the potential of patches, the needed kinetic variables and the resulting types of collision. Section 3 presents how to find the point of contact of real collision and the time needed to arrive at this point. Section 4 describes the numerical part and Section 5 finally provides the expressions and conditions for momentum transfer. In Section 6 the molecular simulation results for two chosen starting configurations are presented and, finally, in Section 7 the summary is given.

2. The potential interaction, kinetic variables and types of collision

Within the framework of the patch–patch center model (PPC), we consider a two-dimensional system composed of large colloidal spherical particles of the radius R and diameter D , whose surface is decorated with the interacting spots. The interaction potential between the spots follows the rule

$$V = \begin{cases} \infty, & r_{\text{spot}} = 0 \\ V_0, & 0 < r_{\text{spot}} < u_0 \\ 0, & \text{otherwise} \end{cases} \quad (1)$$

where r_{spot} here is counted from the center of the spot (not from the center of the large colloidal particle) to the center of another spot. Let the position of the k^{th} spot belonging to the i^{th} particle be $\mathbf{p}_i^k$.

The state of a particle is given by the position of its mass center $\mathbf{r}$ and its orientation is given by the unit vector along the main axis, $\mathbf{a}$. The main axis can be chosen due to the symmetry of the spots on the surface or arbitrarily (see Fig. 1).

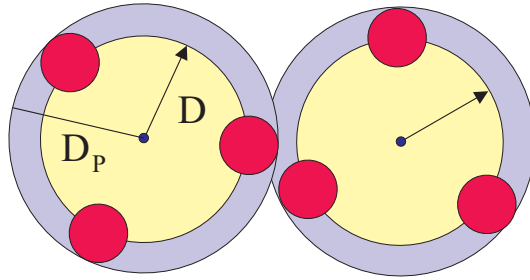


Fig. 1. The patchy spherical colloid. The inner circle is the hard core sphere. The patches sensitive areas are depicted as 3 small circles, the outer ring is called the aureole, its dimension is given by the size of the patch interaction. The aureoles help in finding overlap conditions. The patchy spheres are the objects that are oriented in space — orientations are given by the arrows.

The kinetic state comprises two velocities: linear $\mathbf{v}$ and angular $\mathbf{\Omega}$. If one considers 2D confinement, the angular velocity has only one component along the Z direction, whereas the linear velocity has components along the X and the Y direction.

The particle moves freely both translationally and rotationally. After the time t , its center of mass has the new position $\mathbf{r}'$

$$\mathbf{r}' = \mathbf{r} + \mathbf{v}t \quad (2)$$

and the new orientation $\mathbf{a}'$

$$\mathbf{a}' = \mathcal{R}_x \mathcal{R}_y \mathcal{R}_z \mathbf{a} . \quad (3)$$

In the above, $\mathbf{v}$ is the vector of the linear velocity and $\mathcal{R}_i$ is the rotational matrix about the i^{th} axis with the angle $\alpha_i = \Omega_i t$ with Ω_i being the value of i^{th} component of the angular velocity. The above condition can be used

not only for a constant particle velocity (as well translational as rotational) but also for the case when the time step is small enough that the particle velocity does not change significantly, hence it can be treated as constant.

The word “collision” is used here either for an attractive or repulsive event between two particles. By an attractive event, we mean the spot–spot interaction (note that the result can be either bonding of two particles or dissociation), by a repulsive event, we mean core–core interaction. Two characteristic diameters are considered: D which is the diameter of the true spherical particle and $D_p = D + u_0$ which is the diameter of the sphere of the particle enlarged by the distance u_0 due to the spot potential area.

The collision between two particles can be of five types:

(a) “core” collision

It takes place when the spheres collide as hard bodies and not via spot–spot interaction.

(b) “capture” collision

It is considered when the spot of a particle enters the interacting zone of the other particle spot; as a consequence, the two particles become bonded.

(c) “dissociation”

It is considered when the spot of a particle leaves the interacting zone of the other particle spot; as a consequence, the two particles become unbonded.

(d) “bounce” collision

The particles, which are bonded, reach the border of interacting zones, yet they have not enough energy to break a bond. As a result, a bounce occurs at the border point.

(e) “core–spots” collision

In this peculiar case, the point of contact coincides exactly with the positions of the spots. (As it will be further seen, this collision type, however hard to encounter during the simulations, is very useful while checking consistency of the collisional formulas.)

3. Finding the point of contact and the collision time

In this section, geometrical conditions for the collisions between two patchy particles are considered. Due to the spots presence, they cannot be given by a single formula and need a separate analysis for each situation.

Following the scheme from [19, 20], two particles with orientational degrees of freedom, say i and j , under hard “core” collision touch each other at the point of contact whose position is given by

$$\mathbf{r}_C = \mathbf{r}_i + R\mathbf{u}_i = \mathbf{r}_j + R\mathbf{u}_j. \quad (4)$$

The vectors $\mathbf{u}_i$ and $\mathbf{u}_j$ connect the centers of the mass with the point of collision. As it will be further seen, these two vectors are also among crucial factors that determine the amount of the momentum transfer between two particles. Finding $\mathbf{r}_C$ is one of the first tasks in the event driven molecular dynamic program. At the beginning, let us recall the basic conditions for two hard spheres:

Two spherical particles are approaching each other if the value b_{ij}

$$b_{ij} = \mathbf{v}_{ij} \cdot \mathbf{r}_{ij} \quad (5)$$

is less than zero. In (5), the relative velocity $\mathbf{v}_{ij}$ follows

$$\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j \quad (6)$$

and the relative position vector $\mathbf{r}_{ij}$ is

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j. \quad (7)$$

If the reference frame is fixed to the particle j (Fig. 2), then the particle i will move along the trajectory parallel to the vector $\mathbf{v}_{ij}$. This is also the direction of the vector $\mathbf{s}$, which is the distance to the tangent point of the spheres. In the case of hard spheres, this point will be exactly the point of collision. In the case of hard sphere with an aureole, this denotes the tangent point of two external surfaces of the aureoles and establishes a geometrical condition for considering interactions within aureole's area.

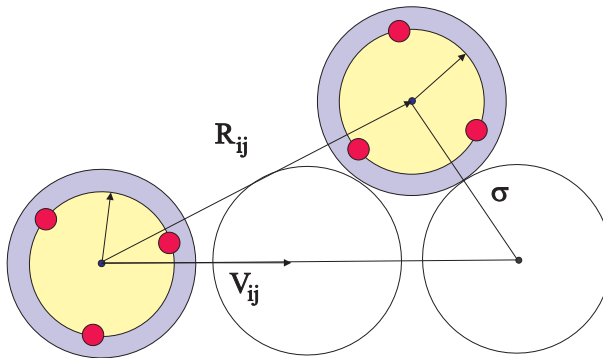


Fig. 2. Geometrical conditions for the freely moving spheres collision.

If $b_{ij} < 0$ holds, then there are two possible geometric points, when the spheres are in contact. To find these points, one considers a triangle built upon the vector of the relative position $\mathbf{r}_{ij}$, the vector of $\mathbf{s}$ and the relative distance between the centers of the spheres in contact (equal to the diameter D). For this triangle, the trigonometric property holds

$$D^2 = r_{ij}^2 + s^2 + 2 r_{ij} s \cos(\varphi) \quad (8)$$

which is a square equation for the unknown s , where φ is the angle between the vectors $\mathbf{r}_{ij}$ and $\mathbf{v}_{ij}$.

Solutions of Eq. (8) give the points of contact

$$s_{1,2} = \frac{-2r_{ij} \cos(\varphi) \pm \sqrt{4r_{ij}^2 \cos^2(\varphi) - 4(r_{ij}^2 - D^2)}}{2}. \quad (9)$$

The smallest root is the closest and the real point of contact. Using (9), the time t_{col} at which the collision takes place can be obtained as

$$t_{\text{col}} = \frac{\sqrt{(\mathbf{r}_{ij} \cdot \mathbf{v}_{ij})^2 - v_{ij}^2 (r_{ij}^2 - D^2)} - \mathbf{r}_{ij} \cdot \mathbf{v}_{ij}}{v_{ij}^2}. \quad (10)$$

Similar equations are obtained, if one considers any movement of the particles from the r_{ij} into r'_{ij} positions. Then, the cosine theorem for a triangle gives

$$r'^2_{ij} = r_{ij}^2 + 2t\mathbf{v}_{ij} \cdot \mathbf{r}_{ij} + t^2 v_{ij}^2. \quad (11)$$

If the new position is to coincide with the point of contact $r'^2_{ij} = D^2$, from (11) one, as expected, obtains also (10).

The formula (10) is characterized by the spheres diameter, so can be applied as well for hard core interacting spheres as for the spheres with aureoles. Introducing the symbol $C^{(s)}_{ij} = r_{ij}^2 - D_{(s)}^2$, where the index (s) can be used to distinguish between the types of spheres (let us use C_{ij} for hard spheres and $C^{(a)}_{ij}$ for aureoles) (10) can be given then as

$$t_{\text{col}} = \frac{-b_{ij} \pm \sqrt{b_{ij}^2 - v_{ij}^2 C^{(a)}_{ij}}}{v_{ij}^2}. \quad (12)$$

C_{ij} can never be less than zero, since this denotes nonphysical overlapping of hard bodies. On the contrary, $C^{(a)}_{ij}$ can be lesser or greater than zero since overlapping of the aureoles zones are allowed. In the latter case, two situations are possible. (a) Two particles are moving toward each other and, consequently, a hard core collision may take place. (b) The separation of two particles is getting larger and the particles sooner or latter will reach the tangent position of two aureoles. Depending on their energy, the particle may separate or bounce. Bouncing means the change of the velocity,

so the particle again move toward each other. It may also look like rattling within the aureoles zones. In view of the future diffusion studies, it is worth noting here that the rattling in cages may cause negative parts in velocity autocorrelations and can substantially influence the diffusional properties.

In order to find the real collision time, the following conditions must be checked:

I. $b_{ij} < 0$ (Spheres are approaching.)

(a) $C_{ij}^{(a)} < 0$ (Aureoles are overlapping.)

(1) $b_{ij}^2 - v_{ij}^2 C_{ij} > 0$ (Cores can collide.)

$$t_{\text{col}} = \frac{-b_{ij} - \sqrt{b_{ij}^2 - v_{ij}^2 C_{ij}}}{v_{ij}^2} \quad (\text{Time to the cores collision.})$$

(2) $b_{ij}^2 - v_{ij}^2 C_{ij} < 0$ (Cores do not collide. Aureoles can be tangent.)

Time condition for the two tangent aureoles follows:

$$t = \frac{-b_{ij} + \sqrt{b_{ij}^2 - v_{ij}^2 C_{ij}^{(a)}}}{v_{ij}^2}.$$

The real time of collision must be found numerically on the basis of the spot-spot distance $|p_i^k - p_j^l| = u0$ (for any spot pair k, l). The above time for the tangent aureoles forms the upper limit for the numerical search.

(b) $C_{ij}^{(a)} > 0$ (Aureoles are not overlapping.)

(1) $b_{ij}^2 - v_{ij}^2 C_{ij}^{(a)} < 0$ (No collision)

(2) $b_{ij}^2 - v_{ij}^2 C_{ij}^{(a)} > 0$ (Attractive collision with capture possible.)

Time condition for the two tangent aureoles follows:

$$t = \frac{-b_{ij} - \sqrt{b_{ij}^2 - v_{ij}^2 C_{ij}^{(a)}}}{v_{ij}^2}.$$

After reaching this time, the condition (a) concerning overlapping aureoles applies. The collision denotes here only capture.

II. $b_{ij} > 0$ (Centers recede.)

(a) $C_{ij}^{(a)} > 0$ (Aureoles are not overlapping. No collision)

(b) $C_{ij}^{(a)} < 0$ (Aureoles are overlapping.)

Time condition for the two tangent aureoles follows:

$$t = \frac{-b_{ij} + \sqrt{b_{ij}^2 - v_{ij}^2 C_{ij}^{(a)}}}{v_{ij}^2}.$$

This time forms upper limit for the numerical search.

III. $b_{ij} = 0$ (Spheres are at a constant distance.)

(a) $C_{ij}^{(a)} < 0$ (Aureoles are always overlapping.)

In this case, the spot-spot interaction can occur because of the particles rotations.

4. Numerical calculations of the real collision times

The aureoles geometry, as presented above, is only additional helpful indication that allows to speed up calculations. In principle, the particles move in straight lines, but, because of rotations, the patches trajectories are no longer linear. To find the point when the two spots are exactly at the distance $u0$, one has to consider the following procedure.

Each point that belongs to the surface of a particle can be described by the formula

$$\mathbf{r}_s = \mathbf{r} + R\mathbf{u}. \quad (13)$$

We are looking for the time when the following condition is fulfilled

$$[\mathbf{r}_i + \mathbf{v}_i t + R\mathbf{u}'_i(t) - \mathbf{r}_j - \mathbf{v}_j t - R\mathbf{u}'_j(t)]^2 = u0^2, \quad (14)$$

where $\mathbf{u}'_i(t) = \mathfrak{R}_x(t)\mathfrak{R}_y(t)\mathfrak{R}_z(t)\mathbf{u}_i$. This equation can be written as $\Psi(t) = 0$, where $\Psi(t)$ is a strongly nonlinear, however a smooth function of time. We can find the solution of Eq. (14) using, for instance, the Newton–Raphson method [21]. The starting time we begin the search at is zero and the closing (bracketing) time is dictated according to the geometrical rules discussed in the previous section (due to the condition of two tangent aureoles). If the minimum of Ψ is reached without fulfilling Eq. (14), then the procedure may stop, if the particles are not fast rotating, because the spots are departing from each other since that moment.

The case of fast rotating particles is a separate problem. In this case, Ψ may exhibit even several extremal points. As it is well known, the standard Newton–Raphson method fails, if the function, whose roots are searched for, exhibits extrema. Several approaches exist to overcome this problem like, for instance, combination of bisection and Newton–Raphson techniques [21]. We propose here also another way. It is presented in Fig. 3.

The standard Newton–Raphson method extends the tangent line at a current point t_i until it crosses zero, then it assumes as the next guess for t_{i+1} just the obtained abscissa of that zero-crossing. The method is fast and powerful unless it encounters extrema. To get close to the root, one has to pass through these extremal points. Let us assume that we go from left to right (just in accordance with the growing time t). We calculate the first derivative at the chosen point t_i to obtain the tangent line and find

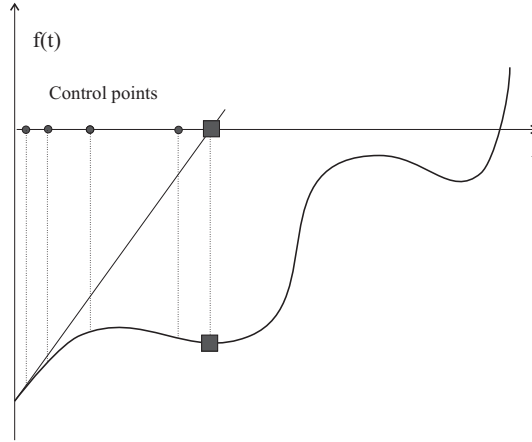


Fig. 3. Double step modified Newton–Raphson method.

the zero-crossing point t_{i+1} . At the same time, we calculate the control points tc_i due to the formula $tc_{i+2} = tc_i + 2 * (tc_{i+1} - tc_i)$ as long as the control point is less than t_{i+1} . If the tangent line does not cross the zero level or leads to the point far from the root (where the function Ψ changes sign), we limit the number of control points to 4 or 5. Checking the values of the derivatives and the function itself, we judge whether a minimum or maximum has been passed, so one can proceed to the regime, where the standard Newton–Raphson method works well.

5. The exchange of momentum and angular momentum during a collision

5.1. Conservation laws

During a collision, both momenta ($\mathbf{P}_i, \mathbf{P}_j$) and angular momenta ($\mathbf{J}_i, \mathbf{J}_j$) of the colliding bodies are changed into new values (denoted with a prime superscript)

$$\begin{aligned} \mathbf{P}'_i &= \mathbf{P}_i + \Delta \mathbf{P}, & \mathbf{P}'_j &= \mathbf{P}_j - \Delta \mathbf{P}, \\ \mathbf{J}'_i &= \mathbf{J}_i + R\mathbf{u}_i \times \Delta \mathbf{P}, & \mathbf{J}'_j &= \mathbf{J}_j - R\mathbf{u}_j \times \Delta \mathbf{P}, \end{aligned} \quad (15)$$

where the exchange of momentum $\Delta \mathbf{P}$ (see Fig. 4) in the case of the interacting patches A and B has the orientation along the line connecting their centers, denoted as $\mathbf{u}_{AB}$ and directed from A to B . During a collision, the momentum and angular momentum must be conserved. The momentum conservation is straightforward from (15) and the angular momentum

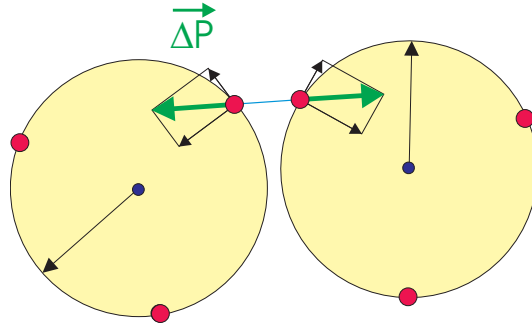


Fig. 4. The momentum transfer under spot-spot interaction. Due to its off-center character, it will influence the rotation of the particle.

conservation can be justified using

$$\mathbf{J}_i + \mathbf{J}_j - R\mathbf{u}_i \times \mathbf{P}_i - R\mathbf{u}_j \times \mathbf{P}_j = \mathbf{J}'_i + \mathbf{J}'_j - R\mathbf{u}_i \times \mathbf{P}'_i - R\mathbf{u}_j \times \mathbf{P}'_j. \quad (16)$$

Applying (15) into the right-hand side of (16), one obtains

$$\mathbf{J}_i + R\mathbf{u}_i \times \Delta\mathbf{P} + \mathbf{J}_j - R\mathbf{u}_j \times \Delta\mathbf{P} - R\mathbf{u}_i \times (\mathbf{P}_i + \Delta\mathbf{P}) - R\mathbf{u}_j \times (\mathbf{P}_j - \Delta\mathbf{P}), \quad (17)$$

which gives exactly the left-hand side of (16).

The unknown value of $\Delta\mathbf{P}$ should be obtained from the energy conservation law

$$\begin{aligned} \frac{P_i^2}{2m} + \frac{P_j^2}{2m} + \frac{J_i^2}{2I} + \frac{J_j^2}{2I} &= \frac{(\mathbf{P}_i + \Delta\mathbf{P})^2}{2m} + \frac{(\mathbf{P}_j - \Delta\mathbf{P})^2}{2m} \\ &+ \frac{(\mathbf{J}_i + R\mathbf{u}_i \times \Delta\mathbf{P})^2}{2I} + \frac{(\mathbf{J}_j - R\mathbf{u}_j \times \Delta\mathbf{P})^2}{2I} \pm V_0, \end{aligned} \quad (18)$$

where m is the mass of the particle and I is its moment of inertia (we assume that the spots do not influence the overall inertness). The last term of (18) should be taken with plus in the case when the particle leaves the potential region (the case of “dissociation”), and with minus when the particle enters the potential region (the case of “capture”). In the case of hard bodies collision, there is no term V_0 at all. The formula (18) holds for elastic collisions. Once such a $\Delta\mathbf{P}$ is obtained, it can be easily extended to the case of inelastic collisions, for instance, by taking a fraction of $\Delta\mathbf{P}$. Such an idea not only leads to the dissipation effect [28, 29] but also to the agglomeration, even without bonding among particles.

The right-hand side of Eq. (18) reads

$$\begin{aligned} & \pm V_0 \frac{(\mathbf{P}_i + \Delta \mathbf{P})^2}{2m} + \frac{(\mathbf{P}_j - \Delta \mathbf{P})^2}{2m} + \frac{(\mathbf{J}_i + R\mathbf{u}_i \times \Delta \mathbf{P})^2}{2I} + \frac{(\mathbf{J}_j - R\mathbf{u}_j \times \Delta \mathbf{P})^2}{2I} \\ &= \pm V_0 + \frac{\mathbf{P}_i^2}{2m} + \frac{\mathbf{P}_j^2}{2m} + \frac{(\Delta \mathbf{P})^2}{m} + \frac{(\mathbf{P}_i \cdot \Delta \mathbf{P})}{m} - \frac{(\mathbf{P}_j \cdot \Delta \mathbf{P})}{m} + \frac{\mathbf{J}_i^2}{2I} + \frac{\mathbf{J}_j^2}{2I} \\ &+ \frac{(R\mathbf{u}_i \times \Delta \mathbf{P})^2}{2I} + \frac{(R\mathbf{u}_j \times \Delta \mathbf{P})^2}{2I} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \Delta \mathbf{P}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \Delta \mathbf{P}}{I}, \quad (19) \end{aligned}$$

so equation (18) reads

$$\begin{aligned} 0 = & \frac{(\Delta \mathbf{P})^2}{m} + \frac{(\mathbf{P}_i \cdot \Delta \mathbf{P})}{m} - \frac{(\mathbf{P}_j \cdot \Delta \mathbf{P})}{m} + \frac{(R\mathbf{u}_i \times \Delta \mathbf{P})^2}{2I} \\ & + \frac{(R\mathbf{u}_j \times \Delta \mathbf{P})^2}{2I} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \Delta \mathbf{P}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \Delta \mathbf{P}}{I} \pm V_0. \quad (20) \end{aligned}$$

The momentum exchange because of the spot-spot interaction is directed along the line connecting spots A and B , so $\Delta \mathbf{P} = \Delta P \mathbf{u}_{AB}$ (see Fig. 4).

Introducing this into (20), we receive

$$\begin{aligned} & \frac{(\Delta P)^2}{m} + \frac{\Delta P (\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{(\Delta P)^2 (R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(\Delta P)^2 (R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I} \\ & + \frac{\Delta P R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{\Delta P R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I} \pm V_0 = 0. \quad (21) \end{aligned}$$

The above equation is of the square type $Ax^2 + Bx + C = 0$ with the coefficients

$$A = \frac{1}{m} + \frac{(R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I}, \quad (22)$$

$$B = \frac{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I}, \quad (23)$$

$$C = \pm V_0. \quad (24)$$

From the two solutions of the above square equation ($\Delta P = \frac{-B \pm \sqrt{\Delta}}{2A}$), one is nonphysical. To justify which solution is the right one, let us now set the collision conditions to the simplified case with $V_0 = 0$ and $\mathbf{u}_{AB} \parallel \mathbf{u}_i$ and $\mathbf{u}_{AB} \parallel \mathbf{u}_j$ (the central collision of two hard spheres). As it is easily seen, the root with $+\sqrt{\Delta}$ leads to nonphysical particles overlapping. Also, if our reasoning is correct, the obtained formula for the momentum exchange in the case when $V_0 \neq 0$,

$$\Delta P = -\frac{1}{2} \mathbf{P}_{ij} \cdot \mathbf{u}_{AB} - \frac{1}{2} \sqrt{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})^2 \pm 4mV_0}, \quad (25)$$

should coincide with the collisional formulas from [22].

Indeed, using $\mathbf{u}_{AB} = \frac{\mathbf{r}_{ij}}{r_{ij}}$ and $b_{ij} = \mathbf{r}_{ij} \cdot \mathbf{v}_{ij}$, one gets

$$\begin{aligned} m\Delta v &= -\frac{m}{2} \mathbf{v}_{ij} \cdot \frac{\mathbf{r}_{ij}}{r_{ij}} - \frac{m}{2} \sqrt{\left(\mathbf{v}_{ij} \cdot \frac{\mathbf{r}_{ij}}{r_{ij}}\right)^2 \pm \frac{4V_0}{m}} \\ &= -\frac{m}{2} \frac{b_{ij}}{r_{ij}} - \frac{m}{2r_{ij}} \sqrt{b_{ij}^2 \pm \frac{4V_0 r_{ij}^2}{m}}, \end{aligned} \quad (26)$$

so

$$\Delta v = -\frac{1}{2r_{ij}} \left(b_{ij} + \sqrt{b_{ij}^2 \pm \frac{V_0 r_{ij}^2}{m}} \right) \quad (27)$$

which agrees with appropriate formulas from [22].

5.2. Final equations

Finally, having done the above testing of consistency, we can write down the momentum exchange for the rotating spheres with patches as follows:

(a) “core” collision

$$\Delta P = -\frac{1}{2} \mathbf{P}_{ij} \cdot \mathbf{r}_{ij} / r_{ij} - \frac{1}{2} \sqrt{(\mathbf{P}_{ij} \cdot \mathbf{r}_{ij} / r_{ij})^2}. \quad (28)$$

It takes place, when the spheres collide as hard bodies, with $r_{ij} = D$. In this case, the particles interact under the center-center assumption, so the angular momentum of each particle is not changed.

(b) “capture” collision

It is considered, when the spot of a particle enters the interacting zone of the other particle spot, as a consequence, the two particles become bonded

$$\Delta P = \frac{-\left(\frac{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I}\right) - \sqrt{\Delta}}{2\left(\frac{1}{m} + \frac{(R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I}\right)} \quad (29)$$

with Δ

$$\begin{aligned} \Delta &= I1 + I2 = \left[\frac{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I} \right]^2 \\ &\quad + 4V_0 \left(\frac{1}{m} + \frac{(R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I} \right). \end{aligned} \quad (30)$$

(c) “dissociation”

It is considered, when the spot of a particle leaves the active zone of the other particle spot; as a consequence, two particles become unbonded. The equation is similar to (29)

$$\Delta P = \frac{-\left(\frac{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I}\right) + \sqrt{\Delta}}{2\left(\frac{1}{m} + \frac{(R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I}\right)} \quad (31)$$

but Δ here must be

$$\Delta = I1 - I2 = \left[\frac{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I} \right]^2 - 4V_0 \left(\frac{1}{m} + \frac{(R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I} \right). \quad (32)$$

It is valid under the condition that $I1 > I2$.

(d) “bounce”

If the above condition $I1 > I2$ is not fulfilled, then the particle will bounce at the inner border of the other particle spot interaction zone. The change of momentum will be given by the formula like (31) with $V_0 = 0$ and $-\sqrt{\Delta}$

$$\Delta P = \frac{-\left(\frac{(\mathbf{P}_{ij} \cdot \mathbf{u}_{AB})}{m} + \frac{R\mathbf{J}_i \cdot \mathbf{u}_i \times \mathbf{u}_{AB}}{I} - \frac{R\mathbf{J}_j \cdot \mathbf{u}_j \times \mathbf{u}_{AB}}{I}\right) - \sqrt{\Delta}}{2\left(\frac{1}{m} + \frac{(R\mathbf{u}_i \times \mathbf{u}_{AB})^2}{2I} + \frac{(R\mathbf{u}_j \times \mathbf{u}_{AB})^2}{2I}\right)}. \quad (33)$$

(e) “core-spots” collision

In this peculiar case, the point of contact coincides exactly with the positions of the spots. (As it has already been shown, this type of collision, however hard to encounter during the simulations, is very useful while checking consistency of the collisional formulas.)

5.3. Comparison between the patch–patch center (PPC) and the Kern–Frenkel model (KF)

The most popular interaction model that has been intensively used so far in studying properties of different patchy systems is the Kern–Frenkel model [23]. This model assumes that on the surface of particles exist small patchy areas, which act as windows (see Fig. 5). If it is possible to draw a line that passes through the windows of two closely positioned particles in such a way that it joins their centers, then the interaction between them is governed

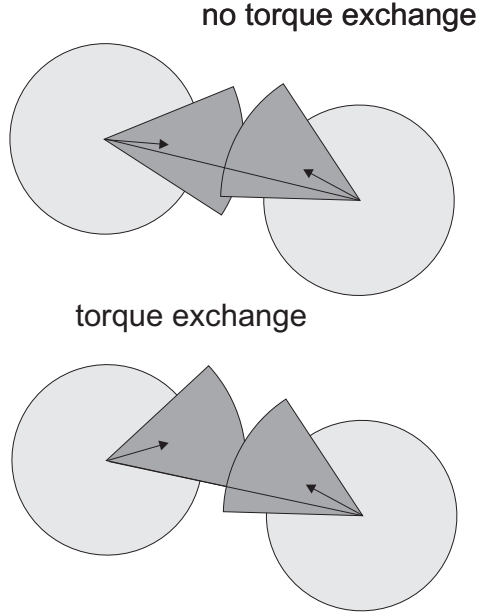


Fig. 5. The Kern–Frenkel interaction of two patchy particles. In the upper case, there is no torque exchange.

by a standard center–center square well potential $V_{\text{SW}}(r_{ij})\Psi(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j)$

$$V_{\text{SW}}(r_{ij}) = \begin{cases} -V_0, & D < r < \lambda D \\ 0, & D > r \end{cases}, \quad (34)$$

$$\Psi(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j) = \begin{cases} 1, & 0 < |\mathbf{u}_i \cdot \mathbf{r}_{ij}| > \cos \theta_0 \\ 0, & \text{otherwise} \end{cases}, \quad (35)$$

where θ_0 is determined by the size of the patch.

How does then the torque occur in such a model? It is connected with the idea how the patch is created — it is cut out from the particle surface by the cone, whose sharp peak is just in the center of the particle. Only in the case when the particles are positioned in such a way that the line joining their centers belongs also to the surface of one of the cones, the condition for the torque exchange is taken into account. This condition is imposed according to the square well potential (34), where the relevant variables are angles. If the patches are small and their number is large, then such situations can be frequently met. When the patches are large and their number is smaller, then the torque exchange becomes less frequent and the dynamics will attain an artificial character. It will be especially significant in the case of Janus particles, when the patch, in fact, is half of the particle surface, hence most of the dynamics will be without a torque exchange at all.

Since almost all of the studies performed so far with the KF potential concern equilibrium properties and phase diagrams, the momentum transfer was not an important issue. Yet, if the dynamical or diffusional properties are concerned, then the KF model will be a reliable choice only when the patches are very small. Also, only then these two models, the KF model and PPC model, are expected to provide a comparable outcome. This conclusion, however, requires more detailed studies.

6. Application of the PPC model formulas to molecular dynamics simulations

On the basis of the above described PPC model, we have performed molecular dynamics simulations for two characteristic initial configurations. As the first case (configuration A, Fig. 6), a perfect hexagonal unclustered system has been chosen and as the second case (configuration B, Fig. 7), an aggregated system is considered. For an aggregated system, we use a configuration that was obtained previously with the help of the Monte Carlo simulations. In both cases, the velocities values were randomly taken from the Maxwellian distribution adjusted to the assumed temperature. This temperature was kept constant throughout all the simulations by the use of the thermostat applied every 200 collisions to compensate for a possible numerical drift. The considered system is relatively small and consists of 480 particles of the diameter $D = 1$ with three symmetrically positioned surface patches. The depth of the square well is equal to $V = 0.05$ and the interaction distance is $u_0 = 0.0595D$. This value ensures that only one bond is possible between two distinct particles. The density is low and equals $\rho = 0.1$ and the temperature is put to $kT = 0.1$. The size of the simulation box for these parameters is equal to $L_{\text{box}} = \sqrt{N/\rho} = 69.57$.

Figure 6 presents typical collision numbers that come from the MD simulations of a hexagonal configuration made of the unbound particles and represents the early stage of the agglomeration process, in which only few dumbbell or triplet structures are being created. The time of simulations corresponds here to 10 000 collisions altogether. In what follows, we will also use the dimensionless time τ in terms of the unit value $\tau_0 = D \frac{m}{kT}$, which corresponds to the time of a particles's free flight over the distance of the diameter D with the averaged velocity corresponding to the temperature kT .

Because of a great difference between core and bounce collisions and capture and dissociation collisions, the logarithmic scale must have been used. At the beginning, when there are no clusters at all, the core collisions are prevailing and no dissociates are present. Yet, when bound structures are being slowly formed, the bounces at the sides of the potential walls occur. They are becoming almost as frequent as core collisions, and after some time,

even more frequent. This latter fact is worth paying special attention, since it is an indicator of the rattling between different points of the patchy well, without hitting the core of the particle. Such an effect will be suppressed in the Kern–Frenkel model due to the potential wall geometry. The number of captures dominates the number of dissociates due to the cluster formation. Note also the fact that all the profiles of the collision numbers in Fig. 6 begin at a nonzero time. This time corresponds to the time interval needed to pass to the first collision in the case, when the system is perfectly hexagonal. It will depend on the initial distribution of the velocities.

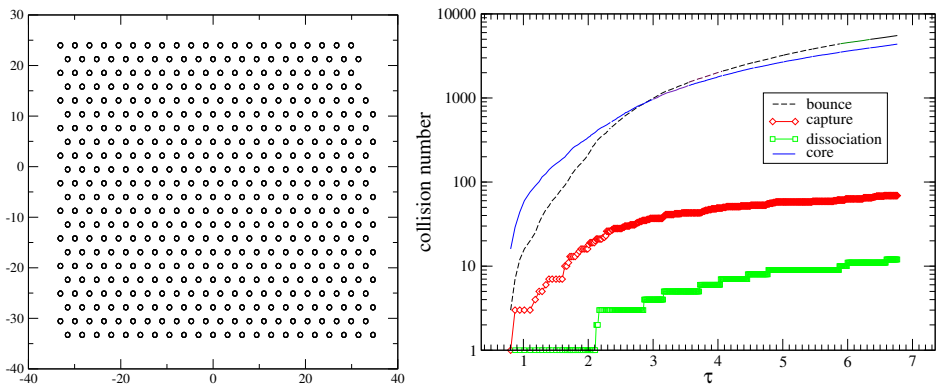


Fig. 6. Collision numbers (right) from a short time dynamics for the bounce, core, dissociation and capture events obtained with the starting configuration of perfect hexagonal order (left).

The MD simulation results for the case of agglomerated particles are shown in Fig. 7. This figure presents the dynamics of collisions inside aggregates. In this example almost all the particles are bound, either by the binding energy or by the positional arrest, hence no longer distance free flights occur within the time of simulation. The overall number of collisions performed is the same as in the previous case (10 000), yet the time associated with this number is about 60 times smaller. Because of the bindings, the simulation can cover only little positional movements (like tremblings) of the particles and confirms that the bounces at the well edges without intermediate core interactions are indeed prevailing. There is also a big difference in the core collision number — it is much smaller than in the first example — at the cost of the bounces. No new captures and only very few dissociates are encountered, which means that within the Monte Carlo simulation the agglomeration process has reached a stable stage.

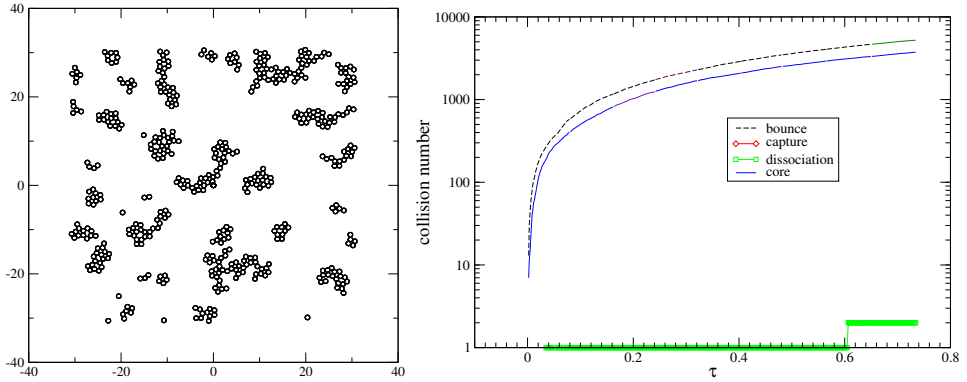


Fig. 7. Collision numbers (right) from short time dynamics for bounce, core, dissociation and capture events for the starting configuration of MC equilibrated system (left).

In Fig. 8, an example of the change of the particles positions that took place within the MD simulation is presented. In the left panel, which is the result of the simulation with the initial hexagonal unbound structure, the configuration bears no longer any resemblance to hexagonal order. One also observes a few dumbbells and one triplet. On the other hand, in the right panel, a change of the particles position within an aggregate is given. Such an aggregate is, in general, a soft and a mobile structure, hence different parts of it may have different mobility. Indeed, parts which are more like chains, especially at the ends of the agglomerate, seem to be softer. Thicker parts, at the same time, look less mobile.

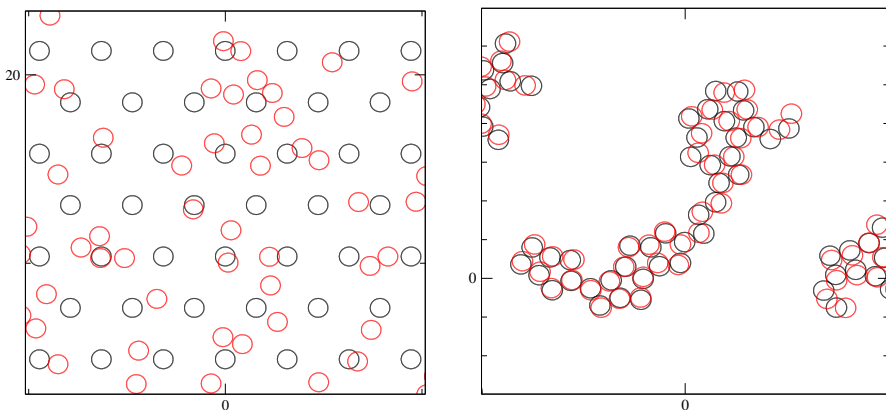


Fig. 8. An example of change of the particles position: black are the particles at the beginning of simulations, gray (red) are the particles after 10 000 collisions. Left panel shows the system A and right panel is for the system B.

It is worth noting that bounces at the walls of the square well potential are prevailing in both above cases, although the number of bonds in the first case is small. This means that the crucial factor responsible for this effect is the curvature of the potential walls.

All the above numerical investigations have been performed under the characteristics of the patches that conform to the condition that two particles may form only one bond, which is realized by tailoring the patches positions on the colloid surface at large distances. The presented interaction model is, however, general and can be used to any architecture of the patches. The assumption of one bond per pair is also the most popular in the studies performed so far. Probably, this is so because of the need to create a firm and stable background of the possible phase diagrams scenarios. Only then, when such background knowledge is collected, extensions of the problem to the case when surface based interactions have more complex geometry, will be justified. As an attempt toward such extensions, one may consider the Monte Carlo investigations concerning cases with a chain of multiple spots placed on the spherical particle equator [8] or in the case of Janus particles [24, 25], where the different interactions are associated with the whole halves of the particles.

7. Summary and discussions

We consider a system of patchy colloids — spherical particles whose surfaces are decorated with interacting patches. Such particles, depending on the state parameters like density or temperature, form agglomerates, the dynamics of which depends strongly on the degree of bonding. A set of formulas for the off-center collisions for the particles interacting via the patch–patch square well potential has been proposed and applied to molecular dynamics simulations. Examples of collisional numbers describing the phenomena of bonding and unbonding — captures and dissociates — and core collisions and bounces at the square well potential walls are given. It has been shown that at the agglomerated state, the dynamics is dominated by the bounces with the potential well borders without hitting cores of the particles.

The importance and validity of the presented PPC model is dictated by the established role of the square well potential as the simplest well model and its place among all other models. With this respect, it reminds the Kern–Frenkel model, yet it assumes more realistic situation, when the interaction centers of the patches are positioned more at the surface of the main particle instead of its center. It is especially important in the case of larger objects like colloids. This assumption, as opposite to the KF model, leads to the ever present torque exchange. This will have an impact on kinetic properties such as diffusional and viscous properties, the heat transfer rate and

spatio-kinetic correlations. It is already known that cluster formation itself causes the viscosity of nanofluid and thermal conductivity to change [26, 27]. If one considers here also hindrance on torque transfer among particles, then the change in relaxation effects of orientational degrees of freedom will be even more enhanced.

The presented model is quite general and can be easily extended to more complex cases. For instance, it can be used as well for elastic as for inelastic collisions, for 2D or 3D particles, for different surface coverage of patches and also it can be extended to particles forming multiple bonds.

The authors thank Prof. Francesco Sciortino, Frank Smallenburg and Paulo Teixeira for their help and encouragement to study patchy colloids.

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