

New molecular approach for the simulation of nanoparticle – polymer interactions: application to the system formed by a lysophospholipidic micelle and polyacrylic acid

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Better understanding of the forces between modified or unmodified nanoparticles would be beneficial for developing new strategies for the production of engineered nanoparticle suspensions, as well as for predicting their fate and transport in the environment. Molecular-level simulations, such as Molecular Dynamics can be useful for understanding the interactions between colloidal nanoparticles, but simulations of very large systems are constrained by the long calculation times and require enormous computer resources. A new computation approach that combines series of cycles of Rigid Body Dynamics and Molecular Dynamics has been applied to the study of the interaction of a lysophospholipidic micelle with polyacrylic acid. The results obtained show that the method makes it possible to reach a stationary interaction structure quite rapidly. The method is ready to be applied to the study of the interaction of a wide range of nanoparticles of industrial, environmental or biological interest via a widely-used and freely-accessible computer code.

Keywords: nanoparticle, micelle, polyacrylic acid, lysophospholipidic micelle, rigid body dynamics, molecular dynamics

Introduction

There are currently more than 900 products on the market that contain nanoscale materials, and the development and commercial production of engineered nanoparticles (ENP) is expected to continue to grow rapidly. Many ENP applications (e.g., as composite materials, components of drug delivery agents, etc.) require ENP suspensions that remain stable in polar media such as water or polymeric resins. However, most ENP are strongly hydrophobic and bare ENP minimize their surface free energy by forming settleable aggregates in solution. To prepare uniform, well-dispersed mixtures, the ENP's exterior surface needs to be modified. Two different methods have been used to stabilize colloidal nanoparticles: either incorporation of functional groups through acid treatment or dispersion by surfactant or polymer adsorption. This means that a better appraisal of the forces between modified or unmodified nanoparticles would help to gain a better understanding of the effects of the above mentioned surface modifications and develop new strategies for producing ENP suspensions. Moreover, the aggregation state of ENP also has a strong influence on their fate and transport in the environment. Understanding the factors governing the aggregation behavior of ENP on its own and in contact with natural particles, surfaces and organic macromolecules, is a key to evaluating their environmental transport, fate and potential interaction with biological species.

Historically, the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been used to describe electrostatic and van der Waals interactions in colloidal systems [1, 2]. However, the

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DLVO theory was originally developed for micron-sized colloidal particles and relies on a continuum approximation that may not extend to nanosized objects. Existing opinions on this issue are contradictory up to this point. On the one hand, results from studies where the functional dependence of the aggregation rates on electrolyte concentration has been measured show that the behavior of nanoparticles follows the qualitative predictions of the DLVO theory in regard to the effect of counterion concentration and valence [3–13]. However, experiments in the literature show that DLVO theory does not always work for micrometer-scale particles at close separations [14–16] and modeling studies indicate that the classical theory might have less predictive power for nanocolloids of less than 10 nm in diameter than for larger particles. For instance, according to Fichthorn and Qin [17, 18], forces that are not taken into account by DLVO theory, such as solvation and depletion, could be very important in colloidal nanoparticle systems.

Molecular-level simulations, such as molecular dynamics (MD), can be useful in understanding the interactions between colloidal nanoparticles. These studies can yield atomic-scale detail and they can be used to resolve the origins and magnitudes of forces between those particles. However, MD simulations on very large systems, such as the ones formed by

several interacting nanoparticles, require very large computer resources which make them prohibitive, even with the current calculation capabilities. To overcome this limitation, we have tested a new strategy that combines series of cycles of Rigid Body Dynamics (RBD) and MD. Its application to the study of the interaction of a lysophospholipidic micelle (LPE) with polyacrylic acid (PAA) is presented here. The same system constructed with explicit water in a parallelepiped box of minimum size would contain more than 120,000 atoms, implying very long calculation times (i.e., when the number of atoms increases in a system, as a consequence, a quadratical increase in the calculation time is observed). The substances used in this study have been chosen only as model compounds with the only objective being to test the new calculation strategy. However, they were not chosen arbitrarily. DLPE is involved in many aspects of living processes [19] and, recently, phospholipid micelles have been used, among other amphiphilic polymers, to encapsulate hydrophobic quantum dot nanoparticles to create water soluble materials suitable for biological applications [20, 21]. Polyacrylic acid (PAA) has been very often chosen as a polymer and polyelectrolyte model substance. A number of industrial processes rely on the use of polyelectrolytes to provoke the flocculation and/or the dispersion of colloidal particles and, in the past decades, the importance of polymer-colloid interaction has also been widely recognized in soil aggregation and pollutant transport in natural waters.

1. Methods

1.1. Computational methods

1.1.1. Molecular Dynamics simulations

In MD, the Newtonian equations of motion are integrated to make it possible to follow the displacement of particles over a certain period of time. This procedure allows the phase space to be sampled and produces a physical dynamic trajectory that permits temporal analysis. MD simulations were performed using the following representation of potential energy:

$$E_{total} = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \sum_{nonbonded} \left[\frac{B_{ij}}{R_{ij}^{12}} - \frac{A_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right] \quad (1)$$

where (i) bond stretching and valence angle deformation are represented by an harmonic potential where K_r and K_θ are the constant forces and r_{eq} and θ_{eq} are reference values; (ii) a torsional term, defined by a set of V_n , n and γ parameters, is associated with the dihedral angles; (iii) the non-bonded interactions are split up into Van der Waals interactions, represented by a Lennard-Jones potential defined by parameters A_{ij} and B_{ij} , and electrostatic interactions modelled by a Coulombic potential. Electrostatic and van der Waals interactions are only calculated between atoms in different molecules or for atoms in the same molecule separated by at least three bonds. MD calculations have been performed using XPLOR [22, 23]. The united-atoms (UA) approach has been used in the calculations. UA force fields for MD simulations provide a higher computational efficiency with little sacrifice in accuracy when compared to

all-atom force fields, especially in aliphatic chain simulations where very few specific interactions exist [24].

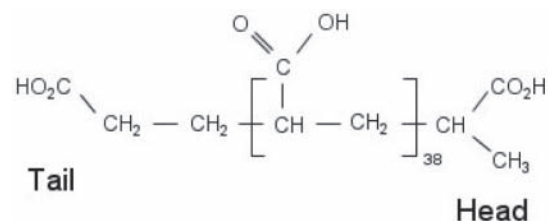
1.1.2. Rigid Body simulations

Rigid Body (RB) dynamics solves Newton equations of motion for rigid collections of atoms. Atoms are grouped into rigid groups, the motion of which is determined by summing the forces acting on all elements of a group and integrating the RB equations of motion. The XPLOR implementation of RB dynamics follows the algorithm described by Head-Gordon and Brooks [25]. This algorithm treats each group as a continuous mass dislocated at the center-of-mass position and characterized by its inertia tensor. Only the non-bonded interactions are computed as RB dynamics energy interactions. However, all atoms are taken into account for the calculation of the general energy. The theoretical details are can be found in the XPLOR manual ([22], pages 136–140).

1.2. Choice of the polymer and micelle models

Polyacrylic acid (PAA) monomers were simulated using a united-atom (UA) approach. Other parameters needed for the UA model were the standard parameters proposed by the Charmm/XPLOR force field for united atoms [27]. Table 1. shows the atomic charges of the protonated PAA polymer chains used in the MD simulations.

The lysophosphatidylethanolamine (LPE) monomer was derived from the crystal structure of dilaurylphosphatidylethanolamine (DLPE) [28] by replacing the fatty acid substituent of the central glycerol oxygen with a hydroxyl group. Atomic charges were computed with semi-empirical quantum chemistry [26]. They are shown in Figure 1. The Kerubin program [29] was used to build the micelle from the LPE monomers.



CH ₃	tail CH ₂	any other CH ₂	CH	C in CO	O	H in HO
-0.35	-0.35	0.15	-0.15	0.16	-0.40	0.64

Table 1. Atomic charges of the protonated PAA polymer chains used in the MD simulations

1. táblázat MD szimulációban használt protonált PAA polimer láncok atomtöltései

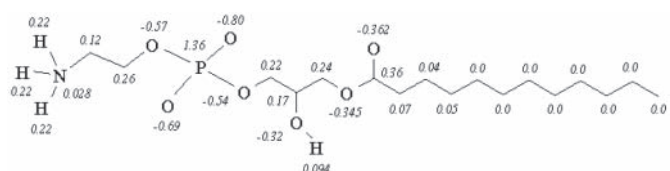
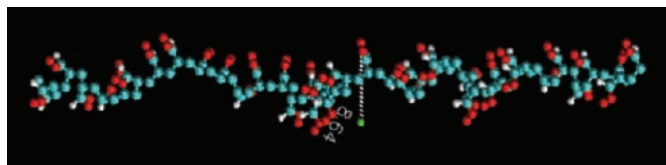


Fig. 1. Formula and atomic charges of the lysophosphatidylethanolamine (LPE) monomers used in the MD simulations

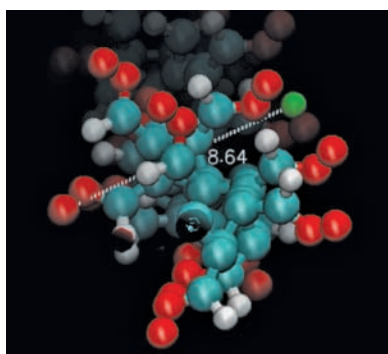
1. ábra Az MD szimulációkban vizsgált lizofatidil-etanolamin (LPE) monomerek összeképlete és atomtöltései

2. Results and discussion

A PAA polymer chain of 40 monomers (330 atoms), all with trans-conformation, was used to create the initial structure of the complex. This polymer chain was immersed in a periodic box of 6516 water molecules ($\epsilon = 1$) and simulated by MD with XPLOR using the UA model for 10 ps. The water molecules of the first hydration shell of the polymer chain (258 water molecules) were kept for later in the simulation of the interaction between the polymer and the micelle.



(a)



(b)

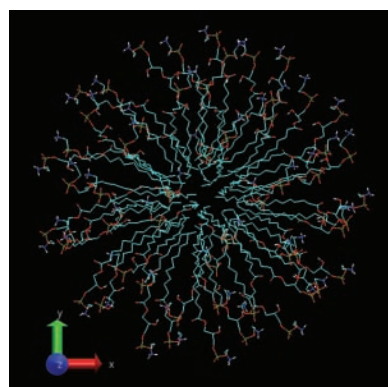
Fig. 2. Longitudinal (a) and cross-section (b) snapshots of the hydrated polyacrylic acid (PAA) polymer build with 40 monomers

2. ábra A 40 monomerből álló hidratált poliakril sav hosszmenti (a) és keresztmetzeti (b) képe

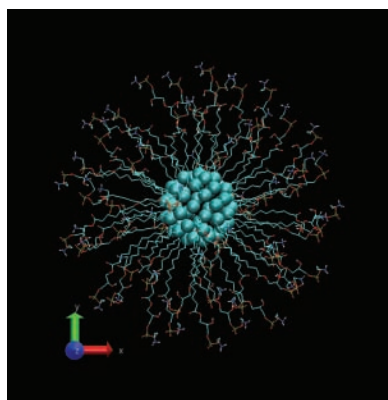
Figure 2. shows snapshots of the hydrated PAA polymer. The simulated PAA has the following dimensions: mean diameter $\sim 8\text{-}9$ Å, hydrated mean diameter = 33 Å, length = 78.6 Å, hydrated length = 105 Å.

A non-charged and equilibrated micelle composed of 56 LPE monomers (2441 atoms) was built with the Kerubin program. The cohesion of the micellar structures is partly due to the interactions between the polar heads of the phospholipid chains of the micelle and water molecules in the first hydration shells. Thus the introduction of explicit water molecules ($\epsilon = 1$) around the micelles is crucial in order to maintain this cohesion during the MD simulations. For this reason, the LPE micelle was equilibrated by 0.1 ps of MD simulation in a spherical box of 2784 water molecules without periodicity. Only 2441 water molecules were kept to hydrate the micelle in further simulations.

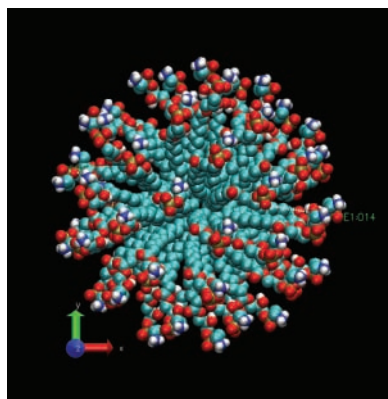
Figure 3. shows snapshots of different steps in the process of building the LPE micelle. The simulated micelle has the following dimensions: mean diameter (from opposite N atoms) = 53 Å, hydrated mean diameter (from opposite N atoms) = 62 Å. Slightly lower diameters are obtained if the distance from opposite P atoms is measured instead. In this case, mean diameter = 50 Å, hydrated mean diameter = 61 Å.



(a)



(b)



(c)

Fig. 3. Snapshots showing different steps in the process of building the LPE micelle: (a) first micelle built up with Kerubin, (b) first minimisation of the LPE, (c) micelle

3. ábra Az LPE micella felépülésének különböző lépéseit bemutató képek (a) az első micella felépülése Kerubin-nel, (b) az LPE első minimalizálódása, (c) a micella

For the RB simulation, two groups of atoms were defined: the hydrated micelle and the hydrated polymer chain. The polymer chain-micelle system included 10 011 atoms. To equilibrate the system, the procedure alternated between RB simulation phases, to displace the micelle relatively to the polymer chain ($\epsilon_{\text{water}} = 80$), and MD simulation phases, to re-equilibrate the water molecules. In order to reduce calculation times, all the atoms of the micelle and of the polymer chain are frozen during each MD phase without modifying the positions of the 'dry' parts of each rigid body obtained in the previous RBD cycle.

Different time step values were tested with two temperature coupling modes [30]. The Langevin method was opted for, since the Berendsen coupling method induced too many temperature fluctuations. Integration times ranging from 1 to 15 fs were tested using this method, and an optimum integration time of 5 fs was finally chosen. The alternating RB/MD cycles lasted for 10 ps and included four successive series of 2.5 ps RB and 50 fs MD with an integration step of 1 fs. *Figure 4a* shows temperature fluctuations with a Langevin thermal bath ($\beta = 30$, $T = 300$ K), RBD only. Temperature fluctuations during four successive cycles of RBD and MD calculations are shown in *Figure 4b*; they reflect water reorganisation needed during the short MD runs.

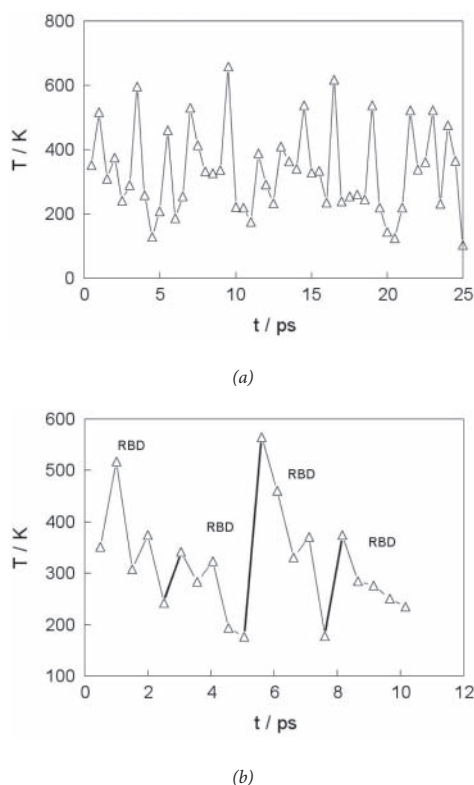


Fig. 4. (a) Temperature fluctuations with a Langevin thermal bath ($\beta = 30$, $T = 300$ K) RBD only. (b) Temperature fluctuations during four successive cycles of RBD and MD calculations

4. ábra (a) Hőmérsékletingadozások a Langevin hőfürdőben ($\beta=30$, $T=300$ K) csak RGB-vel számolva, (b) Hőmérsékletingadozások RBD és MD módszerek kombinációjával számolva, négy egymást követő ciklusban

Quick equilibration of the interaction energies was observed by using the RB/MD method. *Figure 5*. shows the evolution of the non-bonded interaction energies, van der Waals and electrostatic, between the LPE micelle and the PAA polymer chain during four mixing RBD and MD cycles. The initial repulsion, resulting from the arbitrary initial position of the two objects, evolves quite rapidly to a thermodynamic stabilisation. The MD trajectory Van der Waals energy decreases from +2500 to -1000 kcal.mol⁻¹, thus showing good contact reorganisation of the system configuration. Simultaneously, the MD trajectory electrostatic energy relaxes from an initial value of -500 kcal.mol⁻¹ to a more equilibrated value of -100 kcal.mol⁻¹. The evolution of the non-bonded atomic interactions and the temperature fluctuations during the simulations clearly shows that water reorganised itself during MD phases (50 fs).

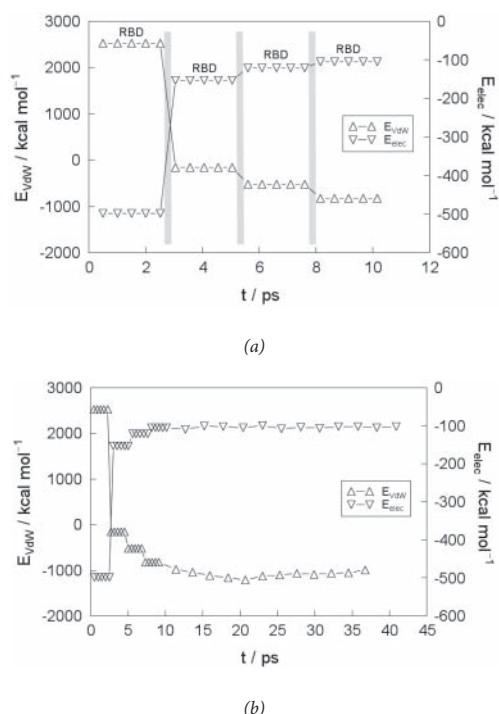


Fig. 5. Evolution with time of the non-bonded interaction energies between the LPE micelle and the PAA polymer chain during (a) the initial four successive cycles of RBD and MD calculations, (b) the complete simulation (40 ps) van der Waals interactions: Δ ; electrostatic interactions: ∇ . RBD (2.5 ps) and MD (50 fs) steps are clearly indicated in (a)

5. ábra Az LPE micella és a PAA polimer közötti nem-kötő kölcsönhatások energiájának időbeli alakulása (a) az RBD és MD módszerek kombinációjával számolva, az első négy egymást követő ciklusban, (b) a van der Waals kölcsönhatások teljes szimulációja (40 ps), Δ ; elektrostatikus kölcsönhatások, ∇ . RBD (2,5 ps) és MD (50 fs) lépések jól láthatók az (a) ábrán

The evolution of the distances from the head and the tail of the PAA monomer to the LPE micelle center is shown in *Figure 6*. Interestingly, the head and the tail of the PAA position themselves at a similar distance from the micelle center at the end of the equilibration. *Figure 7*. shows the evolution of the angles PAA head – micelle – tail PAA (larger angle) and the one formed by two oxygen atoms of the residue 10 of the PAA with the micelle (smaller angle). A correlation between the two angles is observed, as if the micelle rolling over the polymer perturbed them. Finally, a split snapshot of the initial structure of the PAA polymer chain - LPE micelle complex is shown in *Figure 8*.

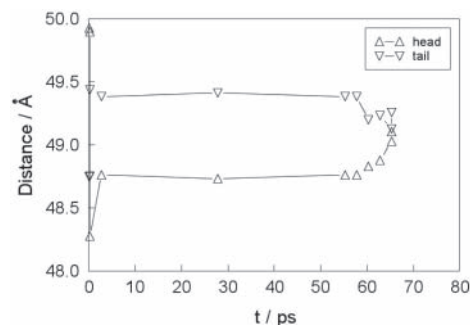


Fig. 6. Evolution with time of the distances from the head (Δ) and the tail (∇) of the PAA polymer chain to the LPE micelle center during four successive cycles of RBD and MD calculations

6. ábra LPE micella középpontja és a PAA polimer lánc fej (Δ), illetve oldal (∇) része közötti távolság változása az idő függvényében az RBD és MD számítások négy egymást követő ciklusában

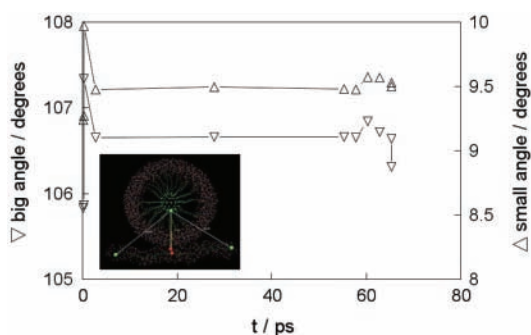


Fig. 7. Evolution of the angles formed by head of the PAA - micelle - tail PAA (big angle) and the OX10 PAA - micelle - OY10 PAA (small angle)

7. ábra A PAA fejrésze - micella - PAA oldalrésze közötti szög (nagy szög) és az OX10 PAA - micella - OY10 PAA közötti szög (kis szög) alakulása

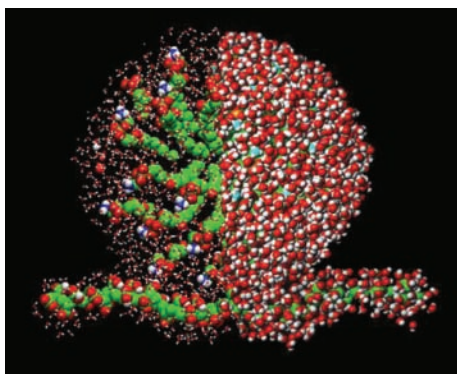


Fig. 8. Snapshot of the initial structure of the PAA polymer chain - LPE micelle complex. At the left hand-side the water molecules are represented in wireframe to clearly show the polymer chain and the micelle monomers. At the right hand-side the water molecules are represented in CPK to show the hydration shell

8. ábra A PAA polimer lánc - LPE micella komplex kezdeti szerkezetének képe. A bal oldalon a vízmolekulákat drótvázal ábrázoltuk azért, hogy a polimer lánc és a micella monomerek jól láthatók legyenek. A jobb oldalon a vízmolekulák CPK-ban láthatók a hidratációs burok bemutatására

In the procedure explained above, the ϵ_{water} was kept at 80, so that the electrostatic energy was screened and a reduced number of water molecules moved simultaneously during the MD steps. This procedure has no effect on the van der Waals energies. Once the dynamic equilibrium was reached, water was allowed to reorganise by performing some calculation cycles with implicit water in all the space for RBD and explicit water ($\epsilon_{\text{water}} = 1$) for MD. Since the initial position was not far from the final one, spatial and energetic convergences were very rapid. Kinetic parameters associated with such quick processes are not accessible experimentally, but are easy to determine from the results obtained. In the study system, a half time of about 3 ps was calculated. The effect of the sampling cut-off on the final result was also tested and the smallest value (19 Å) for which results were not affected by the choice was used.

The Constraint Interaction Energy (CIE) and the distance between the two objects were computed at the end of the simulation. The corresponding value of the van der Waals energy (of CIE) between the PAA polymer chain and the LPE micelle ($-10.9 \text{ kcal.mol}^{-1}$) and the distance between the two objects obtained from this calculation (10.6 Å) can be used to estimate the value of the Hamaker constant [31]. The so-called Hamaker-De Boer theory is often used to compute van der Waals interactions between macrobodies. This theory is an

approximate treatment in which the total attraction energy is obtained by pair-wise summation of London-Van der Waals energies between all molecules of the interacting bodies. Retardation is disregarded. A detailed description as well as a discussion of its limitations can be found in Lyklema [32].

Van der Waals energies and the corresponding Hamaker constants have been computed in the Hamaker-De Boer approximation for a host of geometries but expressions for many geometries are still not well-established. The system being studied can be approximated by the expression for the interaction of a sphere with an infinite plane [32]:

$$E_{\text{vdW}} = -\frac{A_{\text{H}}}{6} \left[\frac{r_s}{h} + \frac{r_s}{h + 2r_s} + \ln \left(\frac{h}{h + 2r_s} \right) \right] \quad [2]$$

where: E_{vdW} is the van der Waals energy (J), A_{H} is the Hamaker constant (J), r_s the radius of the micelle (Å) and h the minimum distance between the micelle and the polymer (Å). This gives a value of 4.0×10^{-19} J for the Hamaker constant. However, according to [33], this approximation can only be applied if the ratio between the distance h and the radius of the sphere r_s is ≤ 1 (0.4 in our case) and the ratio of the cylinder radius to the sphere radius is larger than 10, regardless of the ratio of the cylinder length to its radius. The second condition is not fulfilled in our case. Thus, the value calculated here for the Hamaker constant can only be considered to be an approximation. The value obtained is close, but slightly higher, than the range of values reported for protein-protein interactions in water ($1.0 \times 10^{-20} - 3.6 \times 10^{-20}$ J) [34-40]. It should be mentioned that Rosenfeld and Wasan [41] have put forward an expression for the interaction between a finite cylinder and a sphere. However, we found an error in relation to the integration domain of their expression when we tried to implement it in Mathcad. Since the objective of this study was to show the capabilities of the modeling approach rather than to calculate an accurate value of the Hamaker constant for the given model system, no further effort was devoted to correcting the equation.

3. Conclusions

The results obtained show that the combination of RBD and MD in an explicitly partially hydrated system is a powerful tool for studying interactions between heterogeneous systems because they make it possible to perform complex calculations while keeping calculation times reasonable. It should be pointed out that the same system constructed with explicit water in a parallelepiped box of minimum size contains more than 120,000 atoms. Although it can be solved by using computer codes such as XPLOR [22, 23], VMD [42] and NAMD [43], the high number of atoms present makes the calculation long and the calculation procedure cumbersome because it requires files of structures and atom coordinates be written in hexadecimal notation and the calculation be run by using it.

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Nanorészecske-polimer kölcsönhatások új molekuláris megközelítése: alkalmazási példa lizofoszfolipid micella-poliakrilsav rendszerre

A módosíthatlan vagy módosított nanorészecskék közötti erők jobb megértése előnyösen járulhat hozzá olyan új stratégiák kifejlesztéséhez, amelyek egyrészt alkalmasak előre tervezett tulajdonságú nanorészecske szuszpenziók előállítására, másrészt ezen anyagok környezeti mozgásának és lebomlásának nyomonkövetésére. A molekula szintű szimulációk, köztük a Molekula Dinamika (MD), nagyban elősegíthetik a koloid nanorészecskék közötti kölcsönhatások értelmezését. Ugyanakkor e módszerekkel nagyon nagy rendszerek nem modellezhetők, különleges számítástechnikai háttérigényük, és a számításokhoz szükséges hosszú idő miatt. Közleményünkben egy új, a Merev Testek Dinamikájának (RBD) és a Molekula Dinamikájának kombinált ciklusain alapuló számítási módszer alkalmazását mutatjuk be lizofoszfolipid micellák-ból és poliakrilsavból álló rendszerre. Eredményeink szerint a módszerrel viszonylag gyorsan el lehet jutni a stationárius kölcsönhatás-szerkezetekhez. Módszerünk alkalmas lehet környezeti, vagy biológiai szempontból érdekes, legkülönbözőbb nanorészecskék kölcsönhatásainak tanulmányozására, egy széles körben használatos és szabadon hozzáférhető számítógépes program segítségével.

Kulcsszavak: nanorészecske, micella, poliakril sav, lizofoszfolipid micella, merev test dinamika, molekula dinamika

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SZERKESZTŐBIZOTTSÁGI MEGJEGYZÉS

Az utóbbi két-három évben a korszerű kerámia és szilikát anyagrendszerek területén egyre nagyobb szerephez jut a komplex, szerves és szervetlen anyagokat egyaránt tartalmazó hibridanyagok kutatása és fejlesztése. Ezt jól tükrözi, hogy a 2010. november 14–18. között Oszakában megrendezett 3. Nemzetközi Kerámia Kongresszuson (ICC3) az előadások számát tekintve a hibrid és nano-szerkezetű anyagok kutatása területén elért új eredményeket bemutató 5. Szimpózium a harmadik legnépesebb szekciója volt a rendezvénynek. Ettől több előadást és posztert Japánban csak a korszerű elektrotechnikai kerámia szekció (Szimpózium 6.) és az élenjáró műszaki kerámiák és kompozitok (Szimpózium 14.) tudott felvonultatni. *Lapunkban az Yves Chapron, Alain Porquet és Montserrat Filella szerzők által fentiekben közölt cikkkel szeretnénk az első lépést megtenni a hibridanyagok kutatása, publikálása felé.* Ezek az anyagok gyakran nem csak szerves és szervetlen anyagok szimbiózisából épülnek fel, de olykor egyidejűleg tartalmaznak – vagy tartalmazhatnak – a szilárd kerámia szemcsék és kristályok mellett szerves folyadékokat és/vagy gáz halmazállapotú részecskéket.