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A mesoscopic simulation of material --- Advances in Dissipative particle dynamics research

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Abstract. A mesoscopic simulation of material -- Dissipative particle dynamics (DPD), as the bond between macroscopic and microscopic simulation, had been increasingly draw attention in the research of soft matters, including the flowing condition and the morphological structure. The method of DPD simulation had been applied extensively in the fields of soft matters such as biomacromolecule and the flows of polymers since the DPD simulation has an advantage in time and space scale. In this article, the origin, the theoretical model and the development of dissipative particle dynamics are introduced at first. Subsequently, the advances in the simulation of complex fluids and polymers are reviewed. Finally, the future development and application are concluded.

1 Introduction
Nowadays, the computer numerical simulation is becoming an essential method of solving the intricate problems in technical application and scientific research. Compared with the traditional experiment methods in scientific research, numerical simulation is a more economical and efficient tools, which offer a better way to substitute the expensive, time-consuming and precarious experiments. Meanwhile, computer simulation can provide more specific and substantial information when the results are unable to be directly calculated, observed or obtained by any other way in traditional experiment.

Today the scale of computer simulation is basically divided into three types: microscale (0.1~10nm, 1~10ps), mesoscale (10~1000nm, 10~1000ns), macroscale (>1μm, >1μs). Firstly, the microscale simulation is mainly applied to the research of chemical reaction, structural analysis of molecules and the study in equilibrium structure of simple fluid and dynamics. The main methods of microscale simulation, including Molecular dynamics (MD) and Monte Carlo (MC) etc., are advantaged in the highly scrupulous simulated subject, which can be specialized to the structure in atomic level or molecular level and the details of particle movement, in turns, provide an exact knowledge about the physicochemical property of the micro-morphological structure. But it requires a huge computational expense since the meticulous extent of simulation, especially when study in the dynamic characteristics of soft matter systems, entailing a large computation that hard to be achieved by current computer technology. Secondly, the macroscale simulation is mainly applied to the research of rheological theories and the integral analysis of material processing. Macro-scale simulation methods mainly include the traditional finite element method, boundary element method, finite difference method and so on. Its advantage is that this method can intuitively reflect various macro properties of simulation system. But the drawback is that because of the coarse graining approximation, the simulation may lose some fine structures which are very important. Compared with these two methods given above, mesoscale simulation can be regarded as a bridge of microscopic simulation and macro simulation. It’s valuable
for including substantial details while sharply reducing the calculated quantity and the simulated time. But the fundamental theories of this method actually are still in the stage of development since a lot of research and modification need to be done. Now, the methods of mesoscale simulation are included mesoscopic dynamics (MesoDyn), dissipative particle dynamics (DPD) and etc [3].

The basic idea of DPD is that some individual coarse particles are set to replace the small grain or big grain from the fluid [6]. These coarse particles maintain the Newtonian fluid dynamic in the fluid through the interaction. DPD can achieve bigger spatial scale and longer time scale than the common simulation by integrate the microscopic details’ contribution in the system, while the chemical properties will not be ignored during the coarse graining process. The DPD simulation is using the coarse graining model to simulate the physicochemical property inside and outside the crystal lattice, which is wider use than molecular dynamics simulation and, in certain extent, is closer to the reality as well.

2 Origin of DPD
The method of DPD was firstly proposed by Koelman and Hoogerbrugge in 1992 [1]. Analyzing from the perspective of stimulating objects and numerical integration turn out that DPD is virtually equal to a new molecular dynamic which introduce the soft force and enlarge the spatial-temporal scale. In the DPD stimulation system, a simulated unit, the bead, is not a real atom or molecule but a radical or molecule segment, disposed by the coarse graining process. This bead interacts with other bead base on the soft force. Each bead’s movement represents the collective motion in a tiny area, meanwhile the movement of bead also follow Newton’s laws of motion.

3 Theory of DPD
In the DPD simulation system, the simulation unit is some discrete and coarse-graining beads which have the homogeneous character. Their attributes include mass (m), momentum (P), volume (V). Every bead interacts with other through the soft force in certain extent (cut-off radius), which is shown in Figure 1.

![Fig. 1 Cut-off radius](image.png)

The evolutionary process of bead’s movement accord with the Newton’s equations of motion:

\[
\frac{dr_i}{dt} = v_i, \quad m_i \frac{dv_i}{dt} = f_i
\]

(1)

where \( r_i \) is the site of bead i; \( v_i \) is the velocity of bead i.

For the sake of simplifying the calculation, the mass of every bead are supposed to be equal and nondimensionalized, which is like \( m_i = m = 1 \).
The $f_i$, including conservative force $F_C^i$, dissipative force $F_D^i$, random force $F_R^i$, is the sum of the acting force from other beads towards bead $i$ in the actuating range. Each part of the force is arisen in pairs as equation (2) shown.

$$f_i = \sum_{j \neq i} \left( F_C^i + F_D^i + F_R^i \right)$$

Conservative force ($F_C^i$) is the soft repulsion between the particles that characterize the system. The expression is shown in equation (3).

$$F_C^i = \begin{cases} 
\alpha_{ij} (1 - r_{ij}) r_{ij} & \left( r_{ij} < r_c \right) \\
0 & \left( r_{ij} \geq r_c \right)
\end{cases}$$

$\alpha_{ij}$ is the repulsive force between the particle $i$ and $j$, also known as the conservative force coefficient; the integral of conservative force ($F_C^i$) is the potential function of the simulation system.

4 Complex fluid system
To some newly-developing complex surface catalyst system, DPD simulation can play an irreplaceable part in exploration. For example, it contributes to the study of the Gemini surfactant, which is the combination of two same amphiphilic monomers via spacer group at or near the head group. This kind of systems had been studied sufficiently due to its high surface activity and low critical micelle concentration. Nowadays, its research orientations are concentrated on the dissymmetry Gemini structure and the impact of the monomers, length of the spacer group towards its property and self-assembly.

By applying DPD, Yi Xu et al. have done some primary researches about the self-assembly behavior of the heterogemini surfactant in aqueous solutions [8]. Focusing on five different kinds of heterogemini molecule and its self-assembly behavior, some conclusions are raised as follow according to the DPD simulation. Firstly, the most significant influence on the morphology of self-assembly is the ratio of hydrophilic and hydrophobic segment in the Gemini monomers. The more this ratio difference between two monomers, the more diversity in their self-assembly morphology. Secondly, the length of hydrophilic segment has some influence on the morphology in a certain extent. Because a short hydrophilic segment will lead to some specific morphology. Thirdly, the length of hydrophobic shows the minimal influence, which only affect the concentration of the morphology. Yi Xu et al. utilize DPD simulation to reveal some details about the process of heterogemini surfactant self-assembly, which provide some theoretical guidance for the further study of heterogemini self-assembly and the practical application of this molecule.

In addition, DPD simulation also is involved in the study of oil & water surfactant system. As we all known, increasing the extraction yield of crude oil is vital to the oil production and the additives of surfactant can enhance the extraction yield and stabilize the oil-water emulsion, making the crude separation easier by reducing the surface tension between oil and water. However, reducing surface tension has more positive influence than above on every stage of oil exploitation and the surfactant is the key of it. In order to take better advantage of surfactant during the oil production, several deep researches especially about the interfacial behavior between the oil and the mixed salt solution in the oil reservoir still need to be done. There are still many limitations for current laboratory to study the interface between two immiscible liquids in dissymmetric situation. The special properties and the small size always restrict the experiment. Therefore, using DPD simulation to describe the interfacial behavior is a significant supplement and improvement to these studies.

In some previous DPD simulations, the systems were only confined to some simple structure such as water and organic or water-organic boundary and surfactant.
Recently, some complex coarse oil and surfactant systems were simulated accurately. Hossein Rezaei et al. finished a series of DPD simulations in the interaction behaviors between Perylene imine aromatic hydrocarbons, a surfactant, and water-oil boundary. Therein, the coarse oil system was defined by the model of SARA, which compose of saturated hydrocarbons, aromatic hydrocarbon, resin and pith. Their research applied DPD coarse grained model to calculate the interaction between beads and then simulated the interaction of the arene surfactant with different functional end-group in water-oil interface. What’s more, the aggregating process of water droplet in the coarse oil system was simulated as well. According to the study of Hossein Rezaei et al, firstly with the increase of temperature in the SARA model, the connection between water droplet become closer, which defer the separation of water-oil system [4]. Secondly, at the temperature 298K, aromatic compounds in coarse oil will assemble as a sphere and adsorb the resins on its periphery, while at 363K is the opposite situation. Thirdly, the dispersity of surfactant strengthen with a rise of temperature. Moreover, comparing with four functional end-group of surfactant, the research concluded an optimal choice, offering a vital reference for later study.

5 Complex polymer system

Xin D Guo et al. [7] used DPD to study the phase behavior of paclitaxel loaded amphiphilic copolymer in water and N, N-Dimethylformamide (DMF). The system simulated in this work apply paclitaxel, poly (ethylene oxide)-b-poly(L-lactide) (PEO-b-PLLA) as the amphiphilic copolymer. The copolymer PLLA9 was chosen during the research. Eventually, by varying the solvents composition and the sum fraction of paclitaxel and PLLA9, the simulation found some polymeric micelles possessing different stable structures which include lamella, rod, spherical, hexagonal perforated layers (HPL), dumbbell, homogeneous, bicontinuous. According to the data, a phase diagram of paclitaxel loaded PLLA9 in water and DMF was also mapped by differing the fraction of each component. Consistency of style is very important. Note the spacing, punctuation and caps in all the examples below.

Recently, DPD simulation was firstly applied to study the phase domain architectures evolution for a series of shape memory polyurethanes by Jinlian Hu, Cuili Zhang et al. With different hard segment contents (HSC), the phase structure evolves from from spheres, to linked-spheres, linked-cylinders, then to linked-bi-crossing cylinders at the nanoscale. In short, it was the first time that the 3D nano netpoint-switch-frame architectures which develop from the shape memory polyurethanes with different HSC was substantiated from different phase model.

6 Conclusions

DPD simulation, as a mesoscale simulations technique, become increasingly indispensable method especially in the study of soft-substance system. This method always plays a very important role in whether predicating the property and structure of mesoscale equilibrium state or studying the dynamics of non-equilibrium process. After reviewing the development history of DPD and its applied situation in the study of complex fluid and polymer system, this text can consider that DPD simulation should be improved and optimized in the aspects of interactional potential, improving the integral algorithm and extending the application.

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