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Engineering molecular dynamics simulation in chemical engineering

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HIGHLIGHTS

- Traditional MD is generalized to accommodate discrete elements at different scales.
- Consistency among system, model, software and hardware to achieve high efficiency.
- Possibility of engineering MD into a virtual experiment platform is discussed.

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ABSTRACT

Chemical engineering systems usually involve multiple spatio-temporal scales, grouped into different levels, from the molecular scale of reactants to the industrial scale of reactors. Molecular dynamics (MD) simulation is one of the most fundamental methods for the study of such systems, but it is too costly and hence formidable for simulating large-scale behavior directly. However, there are two great potentials in extending this method. First, the logic and algorithms of traditional MD simulations can be generalized from the material level to higher levels since the elements of each level are all discrete in nature, and can be well defined, allowing an MD-style simulation based on different elements. Second, MD simulations can be accelerated by realizing the structural consistency among the problem, model, software and hardware (the so-called EMMS paradigm). These two potentials give possibilities to engineer the method of MD simulation to deal with the whole spectrum of chemical engineering phenomena.

In this review, we summarize our discrete simulation studies to explore such potentials, from the establishment of a general software and hardware framework, to the typical applications at different levels, including the reactions in coal pyrolysis, the dynamics in virion, the atomic behavior in silicon at millimeter scale, and finally continuum flow. The possibility of engineering MD simulation into a virtual experiment platform is discussed finally.

1. Introduction

Chemical engineering systems typically involve multi-scales, from the material level of atoms, molecules and assemblies to the reactor level of particles and clusters, and then the system level of reactors and processes, as illustrated in Fig. 1 (Li et al., 2009, 2013). Each level features an element scale, a global scale (which is also the element scale of the next higher level) and a meso-scale in between (Li et al., 2009). For example, atoms and molecules are at the element scale of the material level where the bulk of the material corresponds to the global scale and the molecular assemblies in between are at the meso-scale.

Computer simulation is becoming a more and more important approach in chemical engineering with its ever-increasing demand for quantifying such systems in higher accuracy and spatio-temporal resolution, for which experimental methods alone are insufficient in many cases. Molecular dynamics (MD) simulation is one of the most fundamental choices in the toolbox available. In MD simulation, the whole system is discretized into interacting elements, typically atoms, to reflect the underlying mechanism. After more than half a century, it has developed from the study of interacting hard spheres (Alder and Wainwright, 1957) to self-assembly of proteins (Lee et al., 2011; Dill and MacCallum, 2012;

Abbreviations: CPU, central processing unit; CUDA, compute unified device architecture; DEM, discrete element method; DPPC, dipalmitoyl-phosphatidylcholine; EMMS, energy minimization multi-scale; GPU, graphics processing unit; LAMMPS, large-scale atomic/molecular massively parallel simulator; LINCS, linear constraint solver; MD, molecular dynamics; MPI, message passing interface; PE, polyethylene; PPM, pseudo-particles modeling; QM, quantum mechanics; RNA, ribonucleic acid; ReaxFF, reactive force field; SPC, simple point charge; SPH, smoothed particle hydrodynamics; VARxMD, visualization and analysis of reactive molecular dynamics; VPE, virtual process engineering

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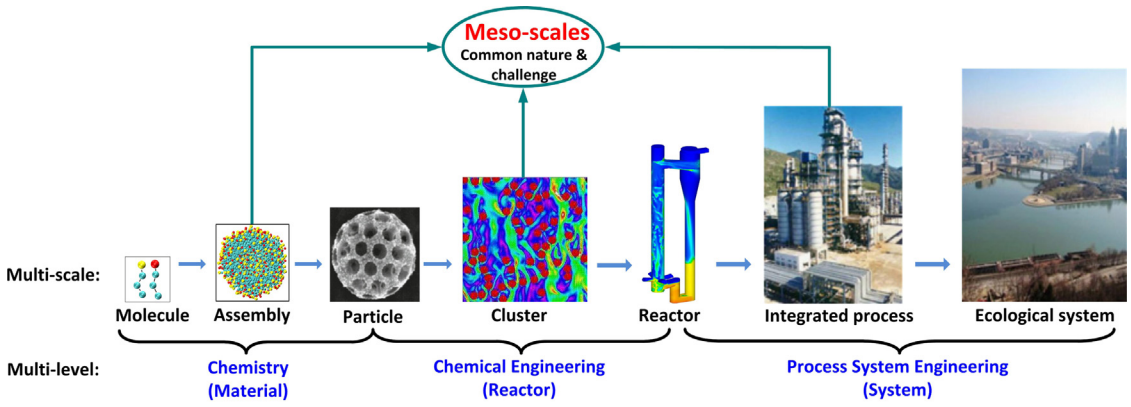

Fig. 1. Multi-scale hierarchy of chemical engineering.
Modified from Li et al. (2009, 2013).

Zhao et al., 2013). Many force fields have been well established to formulate the interactions between the elements, providing fruitful details of the studied systems at the material level.

Although it is computationally formidable to predict macro-scale behavior from atomic scale yet, it can be applied at a much wider scale range and play a more important role, if the principle of MD simulation is understood in a general sense. Thanks to the discrete nature of the physical world, which is organized into multilevels and multiscales, the elements of each level can be described as discrete "particles" with well-defined interaction models, as shown in Fig. 1. Therefore, the framework of MD simulation, that is, discretizing the investigated system into elements with interactions, can be extended to higher levels by substituting the atoms and molecules with the more general "elements" (referred to as "particles" in the following). For example, the discrete element method (DEM) (Cundall and Strack, 1979) and the smoothed particle hydrodynamics (SPH) method (Gingold and Monaghan, 1977; Lucy, 1977) employ natural or fictitious material elements with Newtonian interactions for the simulation of macro-scale behavior. Maybe the essential difference is that, from the modeling aspect, dissipation has to be considered in these interactions, but computationally almost the same algorithmic framework can be used, so that these methods can be "engineered" to become part of the generalized family of MD simulation. That is, the modeling in MD simulation can be generalized from the material level to higher levels. In this review, we will focus on the research of the first two levels in Fig. 1, namely material and reactor systems.

On the other hand, from the computational point of view, a big gap is left between the peak performance of the supercomputers and the sustainable performance of the MD applications (Phillips et al., 2005; Hess et al., 2008), and it is actually not cost-effective to use the mainstream central processing units (CPUs) as the main computing hardware for such applications. The problem can be tackled, from one aspect, by keeping the structural consistency between problem, physical model, numerical algorithm, and hardware (Chen et al., 2009; Ge et al., 2011; Li et al., 2013), which follows the so-called "EMMS paradigm" (Li et al., 2009, 2013; Ge et al., 2011). This paradigm is proposed according to the common features of the multi-scale simulation methods based on the energy-minimization multi-scale (EMMS) model (Li et al., 1988; Li and Kwauk, 1994) and its extensions. The model was first proposed to describe the heterogeneous meso-scale structure in concurrent-up gas–solid flow, featuring the closure of hydrodynamic equations with stability conditions, and then extended to gas–liquid/solid (Liu et al., 2001), gas–liquid (Zhao and Ge, 2007; Yang et al., 2010), turbulence (Li et al., 1999; Zhang et al., 2014) and some other systems (Ge et al., 2007). In this paradigm, the multi-scale simulations start with the prediction of global flow field distribution at the steady state, dynamic evolution of the systems is then followed employing the meso-scale models. In some case, micro-scale details are described by carrying out discrete simulations concurrently. Algorithms with different computational features are then identified and carried out by corresponding processors of different architectures. Higher efficiency and scalability as well as much lower cost can be achieved when this consistency is kept. For the simulation of multiphase flows, this strategy has been proven effective (Ge et al., 2011, 2013; Li et al., 2014a, b).

In the spirit of these conceptions, we will review the studies at our group on the establishment of efficient and scalable MD simulation capabilities, under the name "engineering molecular dynamics simulation". This name stands for both the action of generalizing MD modeling to different scales and levels together with the improving of its implementation, and also the resultant method that is capable of solving engineering problems. A series of applications enabled by this capability, ranging from the reactions in coal pyrolysis, the dynamics in virion, to the atomic behavior in silicon at millimeter scale, until continuum flow, are then revisited to demonstrate the significance of engineering MD simulations in a broader sense.

2. Engineering MD simulation

To engineer MD simulation into a general simulation approach for chemical engineering, it is important to extract the common features and structures of all related methods. For this purpose, we have outlined a flowchart shared by most simulations in the MD-style, as shown in Fig. 2. The general modules in it are also summarized in Table 1, namely, *Neighbor search*, *Interaction processing* and *Configuration update*. In addition, the algorithms for a specific group of methods exclusively are listed as *Particular* modules, which are also shared among them. However, there are still slight functional differences in each general module. For example, in *Neighbor search*, the neighbor-list technique is widely used in traditional MD to accelerate the search of changing neighbors with short-range interactions. In the MD simulation for solid material using many-body potential, a much-simplified fixed neighbor list or even a stencil can be used instead. While in some models of DEM where the interaction contains the history-dependent forces (Zhang and Vu-Quoc, 2000; Rapaport, 2007), the contact history list should be added to the normal neighbor list. However, these variants are interrelated and they can share a lot in implementation and programming. With such abstraction and sharing at different levels, we can minimize the programming efforts in carrying out specific simulation cases. We will discuss the establishment of other modules in the same strategy in the following sections.

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