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THE NUMERICAL ANALYSIS OF SOME SYSTEMS OF DIFFERENTIAL EQUATIONS ARISING FROM MOLECULAR DYNAMICS

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Dedicated to Professor Gheorghe Micula at his 60^{th} *anniversary*

Abstract. Molecular dynamics (MD) has become an important tool in the study of molecules/atoms interaction. In the classical MD, the motion of the atoms is described by the Newton equations, the quantum effects being either neglected or incorporated implicitly in the potential function. In this paper we study the application of MD in the formation of thin films, by an appropriate choice of interacting potentials of Tersof type. The numerical integration is performed by a (parallel) version of the Störmer–Verlet scheme using a particle-in-cell method and nearest neighbor concept. Higher order methods based on composition are also considered.

1. Introduction

Molecular dynamics is a modern computational technique used in condensed matter physics, materials science, chemistry, and other fields, consisting of following the temporal evolution of a system of N particles, interacting with each other by means of a certain law. In classical molecular dynamics, the evolution is based on the Newton's equations of motion and the forces are obtained as gradients of a certain potential which is function of all the particle coordinates.

The MD simulation of coating processes must give both insights into the dynamics of the absorption and growth procedures at the surface layer, and information about the structure of the developing crystal layers. In the first case, one is thus interested in the short time dynamics of the atomic reciprocal effects, while in the second case in the temporal average values of the atomic positions and on variables that depend on it.

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2. Modeling and simulation by molecular dynamics

In molecular dynamics, the behavior of a system of N particles is modeled by Newton's equations of motion

$$\begin{aligned} m_i\ \dot{\mathbf{v}}_i &= -\nabla_i V(\mathbf{r}_1,...,\mathbf{r}_N)\ , \\ \dot{\mathbf{r}}_i &= \mathbf{v}_i\ ,\ 1 \le i \le N\ , \end{aligned} \tag{1}$$

where $\mathbf{r}_i, \mathbf{v}_i$, and m_i stand for the position vector, the velocity vector, and the mass of the i-th particle, and $V(\mathbf{r}_1,...,\mathbf{r}_N)$ refers to the potential energy of the system as a function of the position vectors of all particles. The negative gradient $-\nabla V = -(\frac{\partial V}{\partial x_i}, \frac{\partial V}{\partial y_i}, \frac{\partial V}{\partial z_i})^T$ corresponds to the force $\mathbf{F}_i$ acting on the i-th particle.

We note that (1) represents a Hamiltonian system with respect to the Hamiltonian

$$H(\mathbf{r}_1,...,\mathbf{r}_N,\mathbf{v}_1,...,\mathbf{v}_N) = \frac{1}{2}\sum_{i=1}^{N} m_i\ \mathbf{v}_i^2 + V(\mathbf{r}_1,...,\mathbf{r}_N) \tag{2}$$

which describes the total energy of the system.

The physics of the system is completely determined by the function V which comprises all exterior and interatomar potentials.

For the particular coating processes, suitable choices are Brenner- and Tersoff-type potentials (cf., e.g., [6, 7]) which are of the form

$$V = \frac{1}{2}\sum_{i\neq j} V_{ij} = \frac{1}{2}\sum_{i\neq j} f_C(r_{ij})\ [\ f_R(r_{ij}) + b_{ij} f_A(r_{ij})\ ]\ . \tag{3}$$

Here, $r_{ij} := |\ \mathbf{r}_i - \mathbf{r}_j\ |\ ,\ 1 \le i \neq j \le N$, and $f_C(\cdot)$ is a cut-off function

$$f_C(r) := \begin{cases} 1 & , \quad r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{r-R}{D}\right) & , \quad R - D \le r \le R + D \\ 0 & , \quad R + D < r \end{cases}\ , \tag{4}$$

whereas $f_A(\cdot), f_R(\cdot)$ denote attractive and repulsive potentials, respectively,

$$f_A(R) := -A\ \exp\ (-\lambda_1\ r) \quad , \quad f_R(R) := B\ \exp\ (-\lambda_2\ r)\ . \tag{5}$$

Moreover, the bond-order parameter b_{ij} is chosen as a monotonically decreasing function of the number of neighbors of the atoms i and j according to the bond-order-concept which states that the more neighbors an atom has, the weaker the bond to each neighbor:

$$b_{ij} := (\ 1 + \beta^m\ \xi_{ij}^m\ )^{-\frac{1}{2m}}\ . \tag{6}$$

Here, ξ_{ij} is the effective coordination number given by

$$\begin{aligned} \xi_{ij} &:= \sum_{k\neq i,j} f_C(r_{ik})\ g(\theta_{ijk})\ \exp\ (\lambda_3^3\ (r_{ij} - r_{ik})^3)\ , \\ g(\theta) &:= 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}\ , \end{aligned} \tag{7}$$

where θ_{ijk} represents the bond angle formed by the bond between atom i and atom j and the bond between atom j and atom k.

Note that the weighting factor exp $(\lambda_3^3(r_{ij} - r_{ik})^3)$ takes into account the relative distance between different neighbors: a weaker bond (longer distance r_{ik}) will be considerably more weakened by a stronger bond (shorter distance r_{ij}) than vice versa. Furthermore, the function g, depending on the bond angle, is another weighting factor which is chosen such that it stabilizes the crystallographic structure with regard to shear forces.

Note that the weighting factors do not occur in the classical Tersoff potentials but have been introduced to improve the quality of the model for the specific BN-system under consideration.

The parameters A, B, c, d, h, m, β, and $\lambda_i, 1 \leq i \leq 3$, in (5),(6),(7) are fitted both by using experimentally obtained data such as elasticity modules and lattice specific constants as well as with regard to structural energies (e.g., surface and defect energies) and interatomar forces computed by means of ab-initio quantum mechanical calculations.

Ab-initio methods consider every atom as a many particle system consisting of the atomic nucleus and the surrounding electrons. The many particle system is then solved by self consistent pseudopotential calculations based on the density functional theory. However, such computations require an enormous amount of work and therefore, they have been carried out for less particles than are used in the molecular dynamics approach.

For the numerical integration of the Hamiltonian system (1), symplectic integrators are well suited due to conservation of energy [1]. In fact, a backward analysis [2] shows that the total energy is well preserved for exponentially long time horizons $T = \Delta t \exp(C/2\Delta t)$:

$$\begin{aligned} & H(\mathbf{r}_1(k\Delta t), ..., \mathbf{r}_N(k\Delta t), \mathbf{v}_1(k\Delta t), ..., \mathbf{v}_N(k\Delta t)) \; = \\ = \; & H(\mathbf{r}_1(0), ..., \mathbf{r}_N(0), \mathbf{v}_1(0), ..., \mathbf{v}_N(0)) \; + \; O((\Delta t)^p) \quad , \quad k\Delta t < T \; , \end{aligned}$$

where Δt is the time stepsize and p refers to the order of consistency of the integrator.

We have used a standard symplectic integrator of order $p = 2$, commonly used in molecular dynamics, namely the Störmer–Verlet scheme

$$\mathbf{r}_i(t + \Delta t) - 2\mathbf{r}_i(t) + \mathbf{r}_i(t - \Delta t) = \Delta t^2 \frac{1}{m_i} \mathbf{F}_i(t) \tag{8}$$

which is in fact the most natural discretization of the Newton's equations $m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$.

The two-term recursion (1.8) can now be easily modified to the classical formulation of the Störmer–Verlet schema in molecular dynamics.

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) \; &= \; \mathbf{r}_i(t) \; + \; \Delta t \; \mathbf{v}_i(t) \; + \; \frac{1}{2} \; \frac{(\Delta t)^2}{m_i} \; \mathbf{F}_i(t) \; , \\ \mathbf{v}_i(t + \Delta t) \; &= \; \mathbf{v}_i(t) \; + \; \frac{1}{2} \; \frac{\Delta t}{m_i} \; (\; \mathbf{F}_i(t) \; + \; \mathbf{F}_i(t + \Delta t)) \quad , \quad 1 \leq i \leq N \; . \end{aligned} \tag{9}$$

Thereby, a time loop of the Störmer–Verlet algorithm implementation looks as shown in Figure 1.

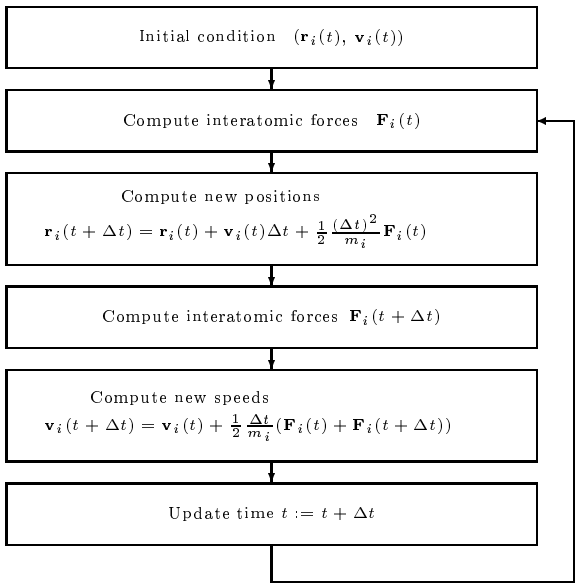

FIGURE 1. Time loop of the Störmer–Verlet algorithm

The Störmer–Verlet method admits an interesting one-step formulation, which is usefull for numerical computations. Introducing the velocity approximation at the midpoint

$$\mathbf{v}_i(t+\frac{\Delta t}{2}) := \mathbf{v}_i(t) + \frac{\Delta t}{2}\frac{1}{m_i}\mathbf{F}_i(t)$$

we get

$$\begin{aligned}
\mathbf{v}_i(t+\frac{\Delta t}{2}) &= \mathbf{v}_i(t) + \frac{\Delta t}{2}\frac{1}{m_i}\mathbf{F}_i(t), \\
\mathbf{r}_i(t+\Delta t) &= \mathbf{r}_i(t) + \Delta t\mathbf{v}_i(t+\frac{\Delta t}{2}), \\
\mathbf{v}_i(t+\Delta t) &= \mathbf{v}_i(t+\frac{\Delta t}{2}) + \frac{\Delta t}{2}\frac{1}{m_i}\mathbf{F}_i(t+\Delta t),
\end{aligned} \tag{10}$$

which is an explicit one-step numerical method

$$\Phi_{\Delta t}^{SV} : (\mathbf{r}_i(t), \mathbf{v}_i(t)) \to (\mathbf{r}_i(t+\Delta t), \mathbf{v}_i(t+\Delta t)) \tag{11}$$

It is interesting to notice that for the implementation of the Störmer–Verlet method, the one-step formulation (1.10) is numerically more stable than the two-term recursion (1.8).

A specific feature, to be dealt with in the following section, is that we have implemented the Verlet algorithm in a parallel setting.

3. *Cell-Partition* Method

The simulation volume is divided into ("*cells* "), congruent subsections filling all the space, in such a way that all neighbours j of a particle i within a distance $r_{ij} < r_c$ are in the same subsection as i or in one of the directly neighbouring subsections. In this way one can limit the computation of reciprocal forces to particles that are in the same and neighbouring subsections. In addition, cubic subsections of edge length r_c can be usually used, the adjustment for the simulation of solids with crystal structure can require other geometry. Figure 2 shows the partitioning for the two-dimensional case.

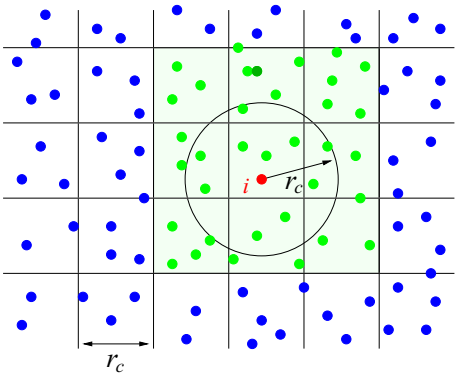

FIGURE 2. of the simulation space (2D)

Neighbour lists

From Figure 2 is evident that particles with a distance $r_{ij} > r_c$ can still be in neighbouring subsections, for which the reciprocal forces were then unnecessarily computed using the *Cell Partitioning* method alone. Therefore, additionally neighbour lists are provided, in which for each particle all next neighbours are seized. For the efficient looking for of the neighbours a appropriately *Cell Partitioning* procedure is used. To make worthwhile the production of the neighbour lists, we must use the same list over several time steps, i.e. we may extend the neighbourhood seize radius not only to neighbours with in a distance $r_{ij} < r_c$, but must increase it introducing a safety distance δ_s (see figure 3). The neighbour lists are valid only during a period $\delta_s/2v_{max}$, for a maximum particle speed v_{max}, because two particles can reduce their maximal distance with the speed of $2v_{max}$), i.e. it must be recalculated again after $[\delta_s/2v_{max}\Delta t]$ time steps.

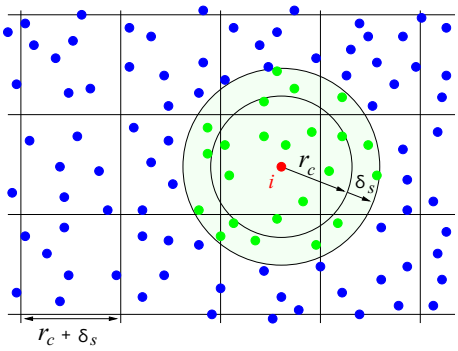

FIGURE 3. Range of the next neighbours (2D)

4. Composition Methods

An interesting procedure for constructing integration methods of higher order is by composition of simple methods. The aim is to increase the order of a simple underlying method, while preserving its desirable properties as symplecticity, symmetry and straightforward implementation. In the following we will use the ideas in [3] and [4], in obtaining a method of order 4 based by the composition of three Störmer–Verlet methods, mainly

$$\Phi_{\Delta t}^{com} := \Phi_{\alpha_1 \Delta t}^{SV} \circ \Phi_{\alpha_2 \Delta t}^{SV} \circ \Phi_{\alpha_3 \Delta t}^{SV} \tag{12}$$

As the Störmer–Verlet method is of order 2, this means $\Phi_{\Delta t}^{SV}$ satisfies (componentwise)

$$\Phi_{\Delta t}^{SV}(\mathbf{w}_0) = \Phi_{\Delta t}^{exact}(\mathbf{w}_0) + C(\mathbf{w}_0)(\Delta t)^3 + \mathcal{O}((\Delta t)^4), \tag{13}$$

where $\Phi_{\Delta t}^{exact}(\mathbf{w}_0)$ denotes the exact flux of the problem. Consequently,

$$\begin{aligned} \Phi_{\Delta t}^{com} &:= \Phi_{\alpha_1 \Delta t}^{SV} \circ \Phi_{\alpha_2 \Delta t}^{SV} \circ \Phi_{\alpha_3 \Delta t}^{SV} \\ &= \Phi_{(\alpha_1+\alpha_2+\alpha_3)\Delta t}^{exact}(\mathbf{w}_0) + \left(\alpha_1^3 + \alpha_2^3 + \alpha_3^3\right) C(\mathbf{w}_0)(\Delta t)^3 + \mathcal{O}((\Delta t)^4). \end{aligned} \tag{14}$$

so, by imposing

$$\begin{aligned} \alpha_1 + \alpha_2 + \alpha_3 &= 1 \\ \alpha_1^3 + \alpha_2^3 + \alpha_3^3 &= 0, \end{aligned} \tag{15}$$

the method $\Phi_{\Delta t}^{com}$ has at least order 3. As the Störmer–Verlet method is symmetric, i.e. $\Phi_{\Delta t}^{SV} = \left(\Phi_{-\Delta t}^{SV}\right)^{-1}$, the composition method will be symmetric if

$$\alpha_1 = \alpha_3. \tag{16}$$

But the order of a symmetric method is always an even number (see [5]), so the method must have at least order 4. Solving the system (15)–(16), we obtain a solution

$$\begin{aligned} \alpha_1 &= 1.3512072 \\ \alpha_2 &= -1.7024145 \\ \alpha_3 &= 1.3512072. \end{aligned} \tag{17}$$

The implementation of this method is straightforward. Once a Stöermer–Verlat (SV) routine is implemented, the composition method consists of calling this routine three times, with different time steps given using the scaling parameters given by (17). This means the method takes two positive intermediate steps $1.3512072 \times \Delta t$ and one negative intermediate step $-1.17024145 \times \Delta t$, as it can be seen from Figure 4.

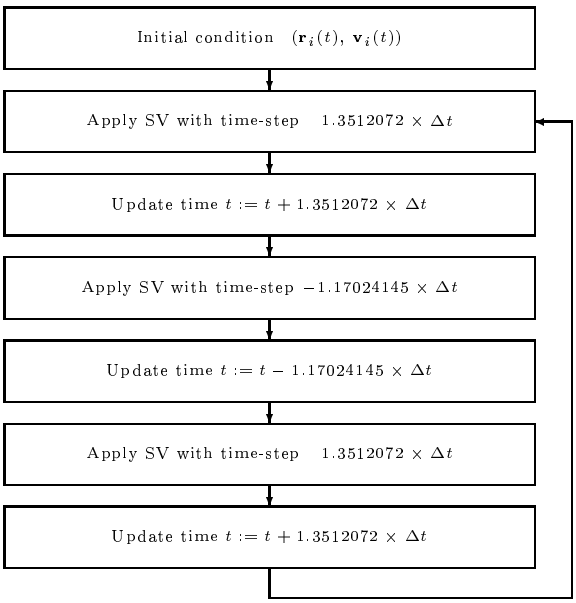

FIGURE 4. Implementation of the composition method

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