A NEW MULTI-PHYSICS MOLECULAR DYNAMICS
FINITE ELEMENT METHOD FOR DESIGNING
GRAPHENE BASED NANO-STRUCTURES

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1 Introduction

Emerging graphene-based structures hold the perhaps highest transformative potential for the composites’ landscape, with worldwide research developing a myriad of novel electronic, structural and coating applications [1]. Hence, simulating the electro-mechanical response of nano-structures is important for a rapidly increasing range of areas.

Continuous progress in nano-synthesis capabilities quickly led to first graphene-based nano-electro-mechanical systems [2], with dimensions from the nano- to the micrometre range. Ongoing efforts have, as recently as May 2013, resulted in the manufacturing of intricate 3D graphene-based nano-structures, such as C_{60} fullerene intercalated graphite [3]. The latter is a prerequisite of a 2013 US patent publication [4] for synthesising carbon nanotube Pillared Graphene Structures (PGS). Calculations predict these PGS to have outstanding mechanical properties, but in three directions simultaneously (e.g. moduli of 0.9 TPa [5]). In addition, Lithium-doped PGS are expected to have unique hydrogen storage capacities above 6 wt %, at ambient conditions [6], due to charge-induced dipoles in the H_{2} by the alkali metal. Hence, PGS potentially represent the first, commercially viable material to meet the US Department of Energy’s requirements for H_{2}-fuelled, mobile applications (e.g. cars, phones, laptops).

At larger, centimetre scales, recent structures such as Aerographite [7], based on micrometre-sized constituent features (i.e. graphene, carbon nanotubes), are among the lightest structural materials to date. At 180 s/m³, Aerographite has unrivalled specific tensile stiffness and strength of 2.57 × 10^{6} and 1.71 × 10^{5} Pa/(kg m³)³, while fully recovering from up to 95 % compressive strain [7].

Concurrently, recent progress in scalable manufacturing and quantification processes permits controlled mass production of graphene structures. Large Chemical-Vapour-Deposition (CVD) polycrystalline graphene, currently possible at the metre scale, was recently shown to have elastic properties identical to pristine graphene [8], paving the way for large-scale TPa-stiffness 2D reinforcements of composite materials (possibly 3D with PGS), as opposed to current 1D GPa-fibre based technology. Techniques for the real-time monitoring of CVD graphene growth [9] and non-destructive rapid evaluation of graphene [10] are available.

This increased ability to precisely synthesise nano-electro-mechanical-systems of varying architectures, and dimensions up to and well beyond the millimetre scale, created a new need for corresponding physically accurate, flexible and numerically efficient modelling methods. Moreover, modelling large giant-covalent-network structures is computationally unaffordable with quantum mechanics or even molecular dynamics methods.

This paper derives a new Molecular Dynamics Finite Element Method (MDFEM) in § 3-5 [11], which exactly embeds the equilibrium equations of Molecular Dynamics (MD) within the computationally more favourable Finite Element Method (FEM). The proposed model has been implemented\(^1\) in a commercial FE code, with both explicit and implicit dynamic formulations, § 6. The implicit MDFEM particularly allows for larger length and time scales as well as eigenvalue analyses. Results and applications, § 7, include conformational and parametric topology studies of PGS, electric field induced polarisations, vibrations and electron-emissions in CNT, electric charge distribution in graphene, as well as a concurrent multi-

\(^{1}\)The software corresponding to this model’s implementation will be made available at: www.imperial.ac.uk/people/silvestre.pinho/researchgroup/members/current/wilmes
scale simulation of CNT fracture with continuum mechanics and MD domains. The novelties of the contributions are discussed in § 8 and § 9.

The proposed multi-physics and multi-scale compatible MDFEM is equivalent to MD, as shown by the analyses of brittle fracture in Carbon Nanotubes (CNT) with defects, but at a considerably reduced computational cost. By modelling buckling, failure, vibrational, piezoelectric and electric-field induced polarisation behaviours, among others, this method can contribute to the design of graphene composites, sensors, H₂ storage and other multi-functional nano-materials.

2 Background

One of the main challenges for nano-simulation models consists of achieving a suitable balance between the accuracy of the physical representation and the scale of numerical applicability.

At one extreme, Ab Initio simulations, for instance based on Density Functional Theory (DFT), can offer high accuracy but cannot readily be used for systems beyond \( O(10^3) \) atoms. At the other extreme, classical Molecular Mechanics (MM) and Dynamics (MD) methods [12–14] only resolve nuclei motion without allowing for chemical reactions or charge redistributions, but may typically be applied to systems with \( O(10^9) \) atoms. Supercomputer simulations have succeeded in increasing this number to \( O(10^{12}) \) atoms [15].

A variety of intermediate theory levels have emerged such as the hybrid DFT-MD Car-Parrinello method [16], or MD force fields based on reactive bond-order potentials [17, 18] and Gaussian-normalised fluctuating charge and polarisable dipole formulations [19].

The MD method has increasingly been incorporated in FEM [20–31] for structural simulations, as the equilibrium equations of MD and FEM can be expressed in equivalent forms. The resulting MDFEM, also referred to as Atomic-Scale Finite Element Method (AFEM) [21], is computationally more favourable than MD [21, 24]. Additionally, MDFEM allows for easier modelling of mechanical loading and, finally, offers a significant increase in compatibility and integrability for concurrent as well as hierarchical multi-scale simulations with larger scale continuum FEM.

MDFEM is applied to the simulation of structural properties, mostly for carbon based nano-structures, due to the maturity and availability of carbon-specific force fields and the large interest in graphene, CNT, and other fullerene derived compounds. However, non-carbon applications have been reported for other nano-structures, such as boron-nitride nanotubes [23] or particulate metal matrix nano-composites [31].

Readily available, structural mechanics FEM elements (e.g. springs, trusses, beams) have been used to represent the deformation of individual bonds when implementing MDFEM [25–30]. However, the use of such structural elements results in detrimental restrictions on MDFEM’s full mechanical non-linear capabilities as well as prohibiting all multi-physics. Namely, it leads to: (i) inadequate element formulations & topologies with limited non-local capabilities; (ii) limited large deformation & multi-physics analysis capabilities; (iii) the inability to perform conformational analyses.

Several MDFEM, which use specifically derived element formulations capable of non-linearities, have been reported [20–23, 32]. However, these element designs vary considerably in their topological complexity and their flexibility in accommodating different force fields, while their implementation does not readily extent to multi-physics.

Finally, a general multi-physics MDFEM has not been proposed yet. It follows that a rigorously derived, exact MDFEM for modelling complex 3D nano-structures across generic load cases, with simplified element topologies, full force field flexibility and straight-forward implementation is required.

The key novel aspects of the proposed model, which represent new contributions to the state of the art, are: (i) a mathematically robust multi-physics derivation; (ii) the formal separation of force field and element topology information; (iii) the ability to differentiate between constitutive, geometrical and mixed constitutive-geometrical instabilities; (iv) a mathematically and numerically optimised implementation; (v) both explicit and implicit FEM formulations, where the latter allows for large time and spacial scales, eigenvalue analyses as well as a singular mass matrix.
3 Multi-Physics Equilibrium

3.1 Hamilton & Lagrange’s Equation

Hamilton’s Principle is a formal and natural approach to describe equilibrium in a discrete multi-physics system and can lead to Lagrange’s equation by a Legendre Transform:

\[
\frac{d}{dt} \left( \frac{\partial (T^*(q))}{\partial \dot{q}} \right)^T + \left( \frac{\partial (V(q))}{\partial q} \right)^T = f, \tag{1}
\]

where the system’s generalised coordinates are denoted by \( q \in \mathbb{R}^{n \times 1} \), while \( f \in \mathbb{R}^{n \times 1} \) represents the corresponding generalised forces and the vector derivatives adhere to the numerator layout convention. The system’s multi-physics conservative generalised potential energy, \( V \), is formally defined as \( V = \int_{\Omega} f_{\text{con}} \, dq = V(q) \), where \( f_{\text{con}} \) denotes selected conservative generalised forces, which may be given in the form of a constitutive relation, i.e. \( \dot{f}_{\text{con}} = \Gamma V(q) \). Eq. (1) implies a choice for \( q \) in an inertial coordinate system, such that the system’s generalised kinetic co-energy, \( T^* \), may only be explicitly dependent on the generalised velocities, \( \dot{q} \in \mathbb{R}^{n \times 1} \), i.e. \( T^* = \dot{T}^* \). The kinetic co-energy is formally defined as \( T^* = \int p \, dq = T^*(q) \), where \( p \in \mathbb{R}^{n \times 1} \) represents the generalised momenta, which are typically expressed in the form of a constitutive relation, i.e. \( p = \Gamma_r(q) \). For energy forms which have no physically defined momentum, the corresponding generalised momenta are considered nil. The generalised potential co-energy, \( V^* = \int f \, dq = V^*(f) \), and the generalised kinetic energy, \( T = \int \dot{q} \, dp = T(p) \), are uniquely related to their respective counterparts by Legendre transforms if the constitutive relations \( \Gamma_V(q) \) and \( \Gamma_r(q) \) are strictly monotonic and hence injective functions. Finally, \( t \) denotes time.

\[\text{Fig. 1. Coordinate system, initial configuration and generalised displacements for atoms } i \text{ and } j.\]

3.2 From Lagrange’s Equation to a Discrete Finite Element Method

In the MD framework, the translational displacements, \( \mathbf{u} \in \mathbb{R}^{n_a \times 1} \) (note: rotational displacements are inappropriate quantities as atoms represent point particles), partial electric charges, \( \mathbf{q} \in \mathbb{R}^{n_a \times 1} \), and electric dipoles, \( \mathbf{p} \in \mathbb{R}^{n_a \times n_d \times 1} \), of all \( n_a \) atoms in an inertial, \( n_d \)-dimensional Cartesian coordinate system constitute an appropriate, comprehensive and natural choice of \( \mathbf{q} \) for a discrete particle system, i.e. \( \mathbf{q} = [\mathbf{u}^T, \mathbf{q}^T, \mathbf{p}^T]^T \). Hence, the corresponding generalised forces, \( \mathbf{f} = [f^T \phi^T \mathbf{E}^T]^T \), are a set of mechanical forces, \( \mathbf{f} \in \mathbb{R}^{n_a \times n_d \times 1} \), point electric potentials, \( \phi \in \mathbb{R}^{n_a \times 1} \), and point electric field values, \( \mathbf{E} \in \mathbb{R}^{n_a \times n_d \times 1} \).

The system, when \( \mathbf{q} = 0 \), is fully defined by the initial position, charge and dipole configuration of all atoms, denoted by \( \mathbf{r} \in \mathbb{R}^{n \times 1} \), so that any current state of the system, \( \mathbf{r} \in \mathbb{R}^{n \times 1} \), may hence be described by \( \mathbf{r} = \mathbf{r} + \mathbf{q} \), see Fig. 1.

For an either linear or non-linear momentum-velocity constitutive relation, \( \Gamma_r(q) \), which leads to an either quadratic or non-quadratic generalised kinetic co-energy, \( T^* \), the latter can always be factorised and expressed in the general form:

\[ T^*(q) = \frac{1}{2} q^T \mathbf{M}(q) \dot{q}, \tag{2} \]

where \( \mathbf{M}(\dot{q}) \in \mathbb{R}^{n \times n} \) is a non-unique matrix which is obtained here as:

\[ \mathbf{M}(\dot{q}) = \frac{2 T^*(\dot{q})}{\| \dot{q} \|^2} \dot{q} \dot{q}^T. \tag{3} \]

This form of \( \mathbf{M}(\dot{q}) \) is guaranteed to yield a symmetric, positive semi-definite matrix. Lagrange’s equation, Eq. (1), may hence be expressed as:

\[ \mathbf{M}(q) \ddot{q} + \left( \mathbf{J}_q V \right)^T = \mathbf{f}, \tag{4} \]

where the generalised potential energy’s Jacobian relative to the system’s displacements is denoted by \( \mathbf{J}_q V \). The generalised mass matrix, \( \mathbf{M}(\dot{q}) \in \mathbb{R}^{n \times n} \), is unique, positive semi-definite, symmetric, may be singular for physics with non-defined momenta, and can be obtained as:

\[ \mathbf{M}(q) = \mathbf{M}(\dot{q}) + \mathbf{D}(\dot{q}) + \frac{1}{2} \mathbf{H}(\dot{q}), \tag{5} \]

with

\[ \mathbf{J}_{ij} = \frac{\partial \mathbf{M}_i(\dot{q})}{\partial q_j}, \quad \mathbf{D}_{ij} = \frac{\partial^2 \mathbf{M}(q)}{\partial q_i \partial q_j}, \tag{6} \]
where \( \mathbf{M} \in \mathbb{R}^{n \times 1} \) denotes the \( j \)th column of \( \mathbf{M} \). The generalised mass matrix, \( \mathbf{M} \), is constant for linear momentum-velocity relations, \( \mathbf{p} = \Gamma_T \cdot (\mathbf{q}) \) and, in the framework of Newtonian mechanics, the mechanical kinetic co-energy for a point particle MD system, as defined in Fig. 1, leads to a diagonal section in \( \mathbf{M} \), where the diagonal terms correspond to the atoms’ masses.

Eq. (4) suggests an analogy with FEM and can be solved using a Newton-Raphson scheme, thus requiring the potential energy’s Hessian relative to \( \mathbf{q} \), which is defined as:

\[
\mathbf{H}^V_{\mathbf{q}} = \frac{\partial}{\partial \mathbf{q}} \left( \frac{\partial V(\mathbf{q})}{\partial \mathbf{q}^T} \right). \tag{7}
\]

4 Molecular Force Fields

4.1 Sub-Potentials & Partitions

The potential energy, \( V \), is given by MD force fields (e.g. AIREBO [18]) which, generally consist of the superposition of a set, \( S \), of sub-potentials, \( V_S \), which can be further partitioned as:

\[
V(\mathbf{c}) = \sum_S V_S(\mathbf{c}_S) = \sum_{\mathbf{r}_S} \sum_{i=1}^{n_p^S} V_{ij}(c_S^i(\mathbf{r}_S, \mathbf{q}_S^i)), \tag{8}
\]

where \( \mathbf{c} \in \mathbb{R}^{m \times 1} \) represents the \( m \) characteristic variables (e.g. bond lengths and angles) of the force field, and \( \mathbf{c}_S \in \mathbb{R}^{m_S \times 1} \) denotes the \( m_S \) specific characteristic variables required for evaluating the sub-potential \( V_S \). Each sub-potential (e.g. total stretching energy) is further divided into \( n_p^S \) repeating partitions (e.g. all bonds in the system) where \( V_S^j = V_S \) in partition \( i \) and zero elsewhere. Hence, \( \mathbf{r}_S^i \in \mathbb{R}^{n_r^i \times 1} \) and \( \mathbf{q}_S^i \in \mathbb{R}^{n_q^i \times 1} \) are the \( n_r^i \) components of \( \mathbf{r} \) and \( \mathbf{q} \) which are necessary for evaluating \( \mathbf{c}_S^i \in \mathbb{R}^{m_r^i \times 1} \), and subsequently \( V_S^i \) in partition \( i \). The partitioning pattern varies for different sub-potential domains, being either a summation over bonds, atoms, angles or charges.

A vast literature giving variable-defining sketches, see Fig. 2, with corresponding definitions is available [14]. For instance, the commonly used \( r_{ij} \) and \( \theta_{ijk} \) in Fig. 2 are defined as:

\[
r_{ij} = \| \mathbf{r}_j - \mathbf{r}_i \| = \| \mathbf{x}_j + \mathbf{u}_j - \mathbf{x}_i - \mathbf{u}_i \|, \tag{9}
\]

\[
\theta_{ijk} = \arccos \left( \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{ik}}{r_{ji} r_{ik}} \right). \tag{10}
\]

Fig. 2. Selected force field characteristic variables.

It is always possible to express any force field (e.g. classical, reactive bond-order, charge-dipole), in the form of Eq. (8). Scalar vector products represent convenient characteristic variables, although complicated functions such as the many-body bond-order variable of reactive fields [17] (usually \( \beta \)), or charge-dipole interaction tensors (usually \( T_{pq} \)) of charge-dipole fields can also be considered as characteristic variables.

4.2 Mechanical Force Fields

Classical force fields include sub-potentials for different deformation modes (e.g. bond stretching, torsion), with some force fields having further sub-potentials for mixed-mode deformations (e.g. stretch-bend in MM3 [12]). Single-mode sub-potentials (e.g. stretch) typically depend on a single characteristic variable, \( m_1^S = 1 \), while mixed-mode sub-potentials (e.g. stretch-bend) may depend on two or more variables, \( m_1^S \geq 2 \).

As an example, the non-reactive Lobo-Keating force field [13], which is fitted against phonon frequencies in graphite, can be expressed as:

\[
V_{L.K.} = V_S(\mathbf{c}_S) + V_B(\mathbf{c}_B) + V_I(\mathbf{c}_I)
\]

\[
= \frac{1}{2} \sum_{i=1}^{n_a} \sum_{j=1}^{3} \frac{\alpha}{4 r_0^2} \left( r_{ij} \cdot r_{ij} - r_0^2 \right)^2 + \sum_{i=1}^{n_a} \sum_{j=1}^{3} \sum_{k=1}^{3} \frac{\beta}{2 r_0^2} \left( r_{ij} \cdot r_{ik} + \frac{1}{2} r_0^2 \right)^2 + \sum_{i=1}^{n_a} \gamma (d_i \cdot d_i), \tag{11}
\]

where \( V_S \), \( V_B \) and \( V_I \) refer to the stretch, bend and inversion sub-potentials, while \( r_0 \) and \( d_i \) denote the natural bond length and dangling bond vector [13]. The latter is defined as \( d_i = r_{ij} + r_{ik} + r_{il} \) with \( j, k, \) and \( l \) being the three neighbour atoms to \( i \), while \( \alpha \), \( \beta \) and \( \gamma \) are fitting parameters. The scalar quantities \( r_{ij} \cdot r_{ij}, r_{ij} \cdot r_{ik} \) and \( d_i \cdot d_i \) constitute a convenient choice as the characteristic variables \( c_S, c_B \) and \( c_I \).
A particularly interesting reactive force field is the REBO potential [17], which is of the form:

\[ V_{\text{REBO}} = \sum_{i=1}^{n_a} \sum_{j>i}^{n_a} \left[ V_R(r_{ij}) - \bar{b}_{ij} V_A(r_{ij}) \right], \tag{12} \]

where \( V_R \) and \( V_A \) represent the repulsive and attractive atomic interactions respectively. The bond order, \( \bar{b}_{ij} \), is a highly non-linear and non-local function of: (i) the bond length \( r_{ij} \); (ii) the bond angles centred at atoms \( i \) and \( j \); (iii) the coordination number of atoms \( i \) and \( j \); (iv) the coordination number of the first and second neighbours to atoms \( i \) and \( j \).

The complexity of REBO arises as \( V_R \), \( V_A \) and \( \bar{b}_{ij} \) are in turn dependent on piece-wise-defined angular functions, \( G(\cos(\theta_{ij})) \) and cut-off functions, \( f^c(r_{ij}) \), where the latter is expressed as:

\[ f^c(r_{ij}) = \begin{cases} \frac{1}{2} \left[ 1 + \cos \left( \frac{\pi}{2} \frac{r_{ij} - D_{ij}^{\text{min}}}{D_{ij}^{\text{max}} - D_{ij}^{\text{min}}} \right) \right] & \text{for } r_{ij} < D_{ij}^{\text{min}}, \quad D_{ij}^{\text{min}} \leq r_{ij} \leq D_{ij}^{\text{max}} \quad \text{and} \\
0 & \text{for } r_{ij} > D_{ij}^{\text{max}} \end{cases}, \tag{13} \]

for \( r_{ij} < D_{ij}^{\text{min}}, \quad D_{ij}^{\text{min}} \leq r_{ij} \leq D_{ij}^{\text{max}} \) and \( r_{ij} > D_{ij}^{\text{max}} \) respectively, with \( D_{ij}^{\text{min}} \) and \( D_{ij}^{\text{max}} \) referring to some of the fitting parameters [17].

### 4.3 Charge & Dipole Force Fields

For multi-physics simulations, the following charge-dipole force field [19], where each atom has an additional nodal charge and electric dipole vector \( \mathbf{D} \), is of particular interest:

\[ V_{\text{Q.P.}} = \frac{1}{2} \sum_{i=1}^{n_a} \sum_{j=1}^{n_a} q_i T_{ij} q_j + \sum_{i=1}^{n_a} q_i (\chi_i + \phi_i) - \sum_{i=1}^{n_a} \mathbf{p}_i \cdot \mathbf{E}_i \]

\[ - \sum_{i=1}^{n_a} \sum_{j=1}^{n_a} \mathbf{p}_i \cdot T_{ij}^{\text{dipole}} q_j - \frac{1}{2} \sum_{i=1}^{n_a} \sum_{j=1}^{n_a} \mathbf{p}_i T_{ij}^{\text{dipole}} \mathbf{p}_j, \tag{14} \]

where \( \chi_i \) denotes the Mulliken-Jaffé electronegativity of atom \( i \). The parametrised tensors for the charge, \( T_{ij} \), charge-dipole, \( T_{ij}^{\text{dipole}} \), and dipole, \( T_{ij}^{\text{dipole}} \), interactions are displacement dependent, i.e.:

\[ T_{ij}^{\text{dipole}} = \frac{1}{4\pi\epsilon_0} \text{erf} \left( \frac{r_{ij}}{\sqrt{2}R} \right), \tag{15} \]

resulting in multi-physics coupling effects, with \( R \) and \( \epsilon_0 \) denoting a fitting parameter and the vacuum permittivity. The conservative external potential, \( \phi_i \), and corresponding electric field, \( \mathbf{E}_i \), are embedded in the internal potential energy; consistent with the formal derivation of Eq. (1).

### 5 Molecular Dynamics FEM

#### 5.1 Constituent Tensor Assemblies

Within the FEM framework, it is always possible to deduce a fully accurate, non-linear representation for the global equilibrium, Eq. (4), by defining appropriate individual elements for each sub-potential. Taking advantage of the decomposition of force fields into sub-potentials, Eq. (8), the system’s Jacobian, \( \mathbf{J}^V_q \) in Eq. (4), and Hessian, \( \mathbf{H}^V_q \) in Eq. (7), can be obtained as:

\[ \mathbf{J}^V_q(x, q) = \sum_S \frac{\partial V_S(x, q)}{\partial q} = \sum_S \mathbf{J}_{qS}^V(x_S, q_S), \tag{16} \]

and similarly:

\[ \mathbf{H}^V_q(x, q) = \sum_S \mathbf{H}_{qS}^V(x_S, q_S). \tag{17} \]

Moreover, from the further division of the sub-potential domains into \( n_p^S \) repeating partitions, it follows that \( \mathbf{J}_{qS}^V \) and \( \mathbf{H}_{qS}^V \) can be obtained by first evaluating the local Jacobian:

\[ \mathbf{J}_{qS}^V(x_S, q_S) = \frac{\partial V_S^V(x_S, q_S)}{\partial q_S}, \tag{18} \]

and local Hessian, \( \mathbf{H}_{qS}^V(x_S, q_S) \), in each partition, followed by an assembling process of the type:

\[ \mathbf{J}_{qS}^V(x_S, q_S) = \bigcup_{n_p^S} \left( \mathbf{J}_{qS}^V(x_S, q_S) \right), \tag{19} \]

with an analogous expression for \( \mathbf{H}_{qS}^V(x_S, q_S) \), where \( \bigcup_{n_p^S} \) denotes the FEM-typical assembly operator which assembles the contributions of all \( n_p^S \) Jacobians, \( \mathbf{J}_{qS}^V(x_S, q_S) \in \mathbb{R}^{1 \times n_S^V} \), into the corresponding positions within \( \mathbf{J}_{qS}^V(x_S, q_S) \in \mathbb{R}^{1 \times n} \) and similarly, the contributions of all \( n_p^S \) Hessians, \( \mathbf{H}_{qS}^V(x_S, q_S) \in \mathbb{R}^{n_S^V \times n_S^V} \), into \( \mathbf{H}_{qS}^V(x_S, q_S) \in \mathbb{R}^{n \times n} \). The contribution of each partition to the generalised mass matrix, \( \mathbf{M} \), is similarly assembled.

The numerical solution to the global equilibrium problem, Eq. (4), using an iterative solution scheme requiring the Hessian, Eq. (7), can therefore be obtained trivially using Eqs. (16) to (19), together with suitable element topologies.

5
5.2 MDFEM Element Topologies

The element topology required for each sub-potential, \( V_S(c_S(r_S, q_S)) \), is determined by the respective components of \( c_S \). It follows naturally that an element topology may be created for each individual sub-potential, which is able to supply the necessary characteristic variables \( c_S^i(r_S^i, q_S^i) \) in each partition \( i \) of the sub-potential’s domain. This element is subsequently meshed \( n_p^S \) times following the partitioning pattern. For instance, a stretch sub-potential may require a two-noded element topology, while an angle-based sub-potential may require information from several atoms.

The simplest and most compact element designs are therefore identical to the characteristic variable-defining sketches for each force field, as shown in Fig. 2. A selection of basic element shapes, used by the authors for classical, reactive bond-order as well as polarisable charge-dipole force fields, is shown in Fig. 3. The single-noded element is required to give the system the appropriate mechanical mass, atom electronegativities and interaction with the external electric field during dynamic and polarisable simulations.

The element topologies from different sub-potentials are then superposed when meshing the atomic geometry. The spacial superposition of multiple element topologies outlines a first fundamental difference between the proposed MDFEM and the classical FEM as, in the latter, element superpositioning in the same location is atypical.

Finally, it can be noted that since the characteristic variables are defined in a global frame of reference, the Jacobian and Hessian tensors of these elements do not require a local to global coordinate transformation prior to the assembly operation in Eq. (19).

5.3 Derivation of the Local Jacobian and Hessian Tensors

The manual derivation for the element Jacobian, \( J_{q_S}^{V_S} \), and Hessian, \( H_{q_S}^{V_S} \), proves to be impossible in but the simplest cases. Modern interpreted processing languages (e.g. MATLAB) are increasingly capable of performing rapid derivation of algebraic expressions so that these tensors can be generated symbolically. The computational effort for substituting the explicit characteristic variable definition, \( c_S^i = c_S^i(r_S^i, q_S^i) \), into \( V_S^i = V_S^i(c_S^i) \) and performing the symbolic derivation is small; however, the resulting expression for a single entry of the Jacobian or Hessian can become prohibitively long for the implementation in a compilable language when using higher-order sub-potentials and inverse trigonometric characteristic variables.

More aggravatingly, the direct evaluation of \( J_{q_S}^{V_S} \) and \( H_{q_S}^{V_S} \) compounds and merges the constitutive information of the implemented force field with the geometrical element topology information. However, force field information and element topology properties can be kept uncoupled, see § 5.4, resulting in a feasible numerical implementation and, significantly increased flexibility for combining different energy potentials with different element topologies.

5.4 Decoupling of the Force Field & Element Topology

Noting Eq. (8), the element Jacobian, \( J_{q_S}^{V_S} \), and Hessian, \( H_{q_S}^{V_S} \), omitting the indices \( i \) for clarity of notation, can equally be expressed as:

\[
J_{q_S}^{V_S} = J_{c_S}^{V_S} J_{c_S}^{q_S} ,
\]

\[
H_{q_S}^{V_S} = \left( J_{c_S}^{V_S} \right)^T H_{c_S}^{V_S} J_{c_S}^{q_S} + \sum_{k=1}^{m_S} \left( J_{c_S}^{V_S} \right)_k H_{c_S}^{q_S} ,
\]

where \( J_{c_S}^{V_S} \in \mathbb{R}^{1 \times m_S} \) and \( H_{c_S}^{V_S} \in \mathbb{R}^{m_S \times m_S} \) are the Jacobian and Hessian tensors of the sub-potential relative to the characteristic variables, hereafter termed Potential Jacobian and Potential Hessian. Similarly, \( J_{c_S}^{q_S} \in \mathbb{R}^{m_S \times n_S} \) and \( H_{c_S}^{q_S} \in \mathbb{R}^{m_S \times n_S \times n_S} \) are the Jacobian and Hessian tensors of the characteristic variables relative to the element nodal DoF, hereafter termed Geometric Jacobian and Geometric Hessian.
The Reconstruction Equations, Eqs. (20) and (21), lead to the following advantages:

1. **Reduced Complexity of Derivatives**

More, yet far shorter derivatives have to be obtained symbolically, where each one can be comfortably implemented in a compilable language.

2. **Independent Scaling of Derivatives’ Length**

The entries of $J^V_{qS}$, $H^V_{qS}$, $J^c_{qS}$ and $H^c_{qS}$ scale in length only with either the complexity of $V_S(c_S)$ or $c_S(r_S, q_S)$, but any compound effect is avoided.

3. **Enhanced Computational Performance**

One to two orders of magnitude fewer numerical operations are needed to evaluate $J^V_{qS}$ and $H^V_{qS}$ using Eqs. (20) and (21) than by a direct approach.

4. **Separation of Force Field Potentials from Element Topologies**

Two separately stored library of pre-compiled derivatives for the force fields respectively the element topologies can be developed.

5. **Independent Analysis of Geometrical, Constitutive and Mixed Instabilities**

Finally, the Reconstruction Equations allow for a refined analysis of global instabilities, which may occur during simulations, by offering the possibility to compute the eigenvalues, $\lambda(\cdot)$, of the Hessian in each element $\lambda(H^c_{qS})$. Moreover, the eigenvalues in both the element’s Potential, $\lambda(H^V_{qS})$, as well as its Geometric, $\lambda(H^c_{qS})$, variable space can be obtained. Furthermore, mixed-mode Potential-Geometric eigenvalues can be computed, i.e. $\lambda\left((J^V_{qS})^T H^V_{qS} J^c_{qS}\right)$ and $\lambda\left((J^c_{qS})^T H^c_{qS} J^c_{qS}\right)$. Hence, the simulation time-history of these eigenvalue sets, together with the Spectral Theorem, Weyl’s Inequalities, Sylvester’s Criterion and Sylvester’s Law of Inertia, can help identify the source of an instability. The latter can either be due to an inappropriate or insufficient boundary condition (e.g. rigid body motion, insufficient structural connectivity), a potential instability (e.g. chemical bond breaking), a geometric instability (e.g. unstable or cyclic characteristic variable) or a mixed potential-geometric instability (e.g. buckling). Hence, this MDFEM is well-suited for identifying the specific partition and the sub-potential deformation mode which may have triggered the instability.

6 **Implementation**

The presented formulation was implemented symbolically in MATLAB\(^2\), with an algorithm structure as shown in Fig. 4. A Force Field Library contains a range of potential energy definitions in the form $V(c) = \sum V_S(c_S)$ while an Element Library stores all available characteristic variable definitions, $c = c(x, q)$, as well as element node connectivities. Using these libraries, the requested geometry is generated and meshed with all required elements before the tensors $J^V_{qS}$, $J^c_{qS}$, $H^V_{qS}$ and $H^c_{qS}$ are symbolically derived. The resultant algebraic expression is exported in a FORTRAN-90/95 format, which is suitable for the implicit and explicit FE package ABAQUS\(^3\). The latter allows for customised element types with freely definable topologies and constitutive properties, termed User Elements (UEL). Given nodal variables $(r_S, q_S)$, the UEL must supply each element’s current Jacobian, $J^V_{qS}$, Hessian, $H^V_{qS}$, and mass matrix, $M$, to the FEM solver for assembly.

Finally, and importantly, implementing a new force field constitutes no additional time cost given a comprehensive Element Library. Currently implemented potentials include but are not limited to: MM3 [12], Lobo-Keating [13], REBO [17], AIREBO [18], Q+P iso/aniso [19], Morse [33].

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\(^{2}\)MATLAB R2012a, The MathWorks Inc.

\(^{3}\)ABAQUS 6.12-1, Dassault Systemes Simulia Corp.
7 Applications

7.1 Brittle Failure of Carbon Nanotubes with Defects

The MD study by Belytschko et al. [33], a purely mechanical study (i.e. \( q = u \) and \( f = f \)), investigates the effects of vacancy, Stone-Wales and weakened-bond defects on the constitutive responses and fracture behaviour of CNT. This MD work was chosen as a reference to demonstrate the equivalence of the proposed MDFEM and MD in a highly non-linear environment up to, and including, bond failure. Four carbon nanotubes, armchair CNT(12, 12)/(40, 40), zig-zag CNT(20, 0) and chiral CNT(16, 8), were strained axially to fracture in both static and dynamic implicit FE analyses. Following Belytschko et al. [33], the REBO [17] potential, Eq. (12), is approximated here by a Morse type potential of the form:

\[
V = V_S + V_B = \alpha \left\{ \left[ 1 - e^{-\beta(r_{ij} - r_0)} \right]^2 - 1 \right\} + \frac{1}{2} \gamma \left( \theta_{ijk} - \theta_0 \right)^2 \left[ 1 + \lambda \left( \theta_{ijk} - \theta_0 \right) \right].
\]  (22)

The above potential is equivalent to REBO for strains up to 10% [33], but without suffering from the subsequent camel-back problem in the force-displacement relation, arising from the derivative of the distance cutoff function \( f^e(r_{ij}) \), Eq. (13). The fitting parameters for Eq. (22) are: \( r_0 = 1.39 \text{Å} \), \( \theta_0 = 2.094 \text{rad} \), \( \alpha = 6.03105 \text{nN Å} \), \( \beta = 2.625 \text{Å}^{-1} \), \( \gamma = 9.0 \text{nN Å rad}^{-2} \) and \( \lambda = 0.754 \text{rad}^{-1} \) [33].

For comparison with literature, the constitutive responses are reported in conventional stress-strain format with the stress in pressure units, where the two-dimensional stress is normalised by assuming a CNT wall thickness, \( t_{\text{wall}} = 3.4 \text{Å} \).

The constitutive response of a CNT(20, 0) with a vacancy defect, Fig. 5, obtained by a static implicit analysis, is in excellent agreement with MD [33]. The implicit static analyses for the three other CNT with different defect types showed equally good agreement and took only \( \mathcal{O}(10^4 – 10^5) \) seconds of CPU time on a standard workstation with 3.3 GHz Intel i5-2500 processors.

Equally, for a CNT(40, 40) with a Stone-Wales defect, a failure strain and stress of 13.9% and 98.8 GPa were obtained by a dynamic implicit analysis. These predictions compare well with the reference MD results of 14.2% and 97.5 GPa, differing only by 2.2% and 1.3% respectively, Fig. 5. Moreover, the implicit dynamic solver is able to compute converged dynamic equilibrium points at the onset of, and during fracture. For the presented example, the unconditionally stable backward-Euler time integrator was used, with light dissipation of 5% mass and 5% stiffness proportional Rayleigh damping, in order to stabilise the simulation numerically. Additionally, the crack propagation path is accurately captured, Fig. 6.

In a Stone-Wales defect, a single bond is subjected to a 90° rotation and reconnected in the typical 5-7-7-5 ring configuration which continues to abide the polyhedral formula. This type of defect requires a conformational step to find its energy minimising state, which is shown in Fig. 7, prior to the load application. The overall length of the CNT(40, 40) remained unchanged after the conformational analysis pre-step, demonstrating that this defect only led to a local variation in the displacement field [34].

![Fig. 5. The proposed MDFEM gives constitutive responses equivalent to MD [33], including failure, for CNT of varying chirality with defects.](image)

![Fig. 6. Equivalence in crack initiation and propagation of the proposed MDFEM and full MD [33].](image)
A NEW MULTI-PHYSICS MDFEM FOR GRAPHENE NANO-STRUCTURES

Fig. 7. Formation of a CNT Stone-Wales defect.

7.2 MDFEM Linear Numerical Scaling

The numerical performance of the proposed model was tested by stretching CNT(5, 5) to 5% strain. Continuously larger nanotubes with up to 1 million atoms, having a maximum length of 12 μm, were run on a standard 3.3 GHz Intel i5-2500 quad-core workstation, showing the proposed model’s static implicit formulation scale linearly, Fig. 8.

Fig. 8. MDFEM has linear computational scaling.

7.3 Conformational Analyses: 3D Pillared Graphene Structures

Unlike MDFEM formulations making use of structural elements, this MDFEM’s elements, Fig. 3, can perform conformational analyses to relax structures with only approximate initial positions. The seeding of three-dimensional PGS meshes [35], such as the one in Fig. 9, is mathematically more complex and considerably more computationally intensive than seeding planar graphene or CNT.

The curved 3D PGS must adhere to the polyhedral formula and the Euler-Poincaré characteristic. The initially seeded geometries typically do not represent a system in equilibrium and hence, a conformational analysis is required before any loading is applied. Non-equilibrium systems easily converge to their energy minimising configuration, Fig. 9, if no external forces are applied.

The PGS in Fig. 9, with a CNT(8, 0) pillar, can be used as a representative Unit Cell in order to tessellate more intricate PGS, Fig. 10. All PGS were equilibrated in a static implicit formulation, using the Lobo-Keating potential, Eq. (11), with the following parameters [13], \( r_0 = 1.421 \text{ Å}, \alpha = 15.59 \text{nN Å}^{-1}, \beta = 2.55 \text{nN Å}^{-1}, \gamma = 0.74 \text{nN Å}^{-1} \) and the element topologies in Fig. 3.

As mentioned in § 1, PGS as in Fig. 10 are expected to have outstanding three dimensional mechanical properties with moduli around 0.9 TPa [5]. When doped with Lithium atoms, these nanostructures are predicted to possess unrivalled H\(_2\) storage capacities at ambient conditions [6].

Hence, the proposed model, with its ability to incorporate both advanced mechanical as well as polarisable charge-dipole force fields, § 7.4, is ideally suited to perform parametric topology studies of the homogenised electro-mechanical, fracture and H\(_2\) storage properties of such complex PGS.

Fig. 9. Conformational analyses are readily possible with the proposed MDFEM.

Fig. 10. Conformational analysis of a large PGS.
7.4 Charge Densities & Electric Field Induced Polarisations

A variety of electro-mechanical effects have been reported, such as charge induced mechanical strains in CNT up to failure [36], charge distributions in CNT deposited on substrates [37], pseudomagnetic fields [38], or electric field induced deflections and vibrations of graphene and CNT [39]. These effects can now be modelled within FEM.

In Fig. 11, the charge distribution in a positively charged graphene sheet [40] was obtained using the anisotropic-polarisation charge-dipole force field $Q^+P\text{aniso}$ [19], together with the mechanical AIREBO potential [18]. Charge accumulates along the edges and at the corners, reaching normalised charge densities (relative to the charge at the centre of the sheet) of 7 and 15 respectively, which agrees with literature [40]. The long-range nature of charge-charge and charge-dipole effects increases the computational cost considerably due to the square scaling of interactions.

Fig. 12 shows a CNT subjected to a perpendicular electric field. The latter induces a charge separation in the neutral and insulated CNT, causing an overall polarisation. In the presence of thermal oscillations during finite-temperature simulations, the vibrational amplitudes disturb the perpendicular alignment of the CNT to the field, potentially inducing axially-aligned dipoles, which in turn may spark an electric-field driven buckling [39].

7.5 Eigenvalue Analyses & Multi-Scale MD and FEM Domains

The implicit MDFEM formulation’s eigenvalue analyses can determine vibrational frequencies and mode shapes of molecular devices, such as simply or doubly-clamped CNT, Fig. 13. Experimental results for electric-field induced vibrational frequencies of simply-clamped CNT have been reported [41], and as shown in § 7.2, CNT with corresponding length-scales in the micrometre range can be modelled using a standard workstation.

Finally, the proposed model is well suited for hierarchical and concurrent multiscale coupling with continuum FEM, Fig. 14. This allows for further computational savings with the proposed model conveniently avoiding the need for coupling two separate numerical solvers when simulating continuum mechanics and MD domains.

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**Fig. 11.** Interpolated normalised charge density for a charged 8.5 nm $\times$ 4.8 nm graphene sheet.

**Fig. 12.** Cut-view of the electric-field induced charge polarisation in a neutral, insulated CNT.

**Fig. 13.** First three mechanical vibration mode shapes of a doubly-clamped CNT.

**Fig. 14.** Concurrent continuum FEM & MD simulation of a CNT with a defect during failure onset.
8 Advances to State of the Art

The proposed model is mathematically rigorous, versatile in accommodating different physics, and is formally equivalent to MD when implemented in an explicit FE formulation. Popular MD explicit time integrators such as the Velocity-Verlet algorithm are typically available with readily accessible FEM Newmark-β or Hilber-Hughes-Taylor integrators. Equally, this model may be implemented with an implicit time integrator, requiring a convergence solver (e.g., Newton-Raphson).

Novelties of the proposed implicit MDFEM include numerical stability, larger permissible time-steps and the removed need for defining artificial kinetic co-energies of energy forms with no physical momenta (i.e. allowing a singular generalised mass matrix $M$). Additionally, the required evaluation of the system Hessian, $H_{qq}^V$, allows for eigenvalue analyses (e.g. used to obtain multi-physics vibrational mode shapes). Hence, the proposed model represents a unified formulation of MD bridging from small to large time and spatial scales, while inherently offering convenient multi-scale integration with continuum FEM domains.

The proposed model’s decomposition of the element Jacobian and Hessian, § 5.4, leads to three key novelties. Firstly, this formal separation of potential and geometric relations permits combining different force fields and element topologies, analogously to the separation of element types and constitutive laws in FEM. Secondly, the numerical implementation becomes feasible, and numerically efficient, § 6. Thirdly, the analysis and differentiation of global instabilities into potential, geometrical and mixed instabilities is possible.

The current formulation can be used both for zero and finite temperature simulations. Initial velocity conditions can be seeded as required (e.g. Maxwell-Boltzmann distribution), with the possibility to apply any thermostat mechanism of choice. Further constraints such as linear momentum conservation, charge conservation or periodic boundary conditions can readily be implemented using Lagrange multipliers.

Finally, even though this paper’s primary focus is on fullerene structures, the proposed model is generally applicable to any molecular structure with or without defects and any number of different chemical species.

9 Conclusion

A new Multi-Physics Molecular Dynamics Finite Element Method has been formally derived from first principles and implemented in FEM. The proposed model: (i) has been shown to be exactly equivalent to MD; (ii) has produced novel mechanical and charge-dipole FEM results; (iii) is computationally more favourable than MD with a linear numerical scaling; (iv) offers a broader range of analyses techniques over wider length and time scales; (v) is inherently well-suited for multi-scale; (vi) is readily implementable; (vii) is applicable to any chemical structure with any number of species.

Analogous to the separation of element topologies and constitutive relations in FEM, the proposed model is the first to introduce a formal uncoupling of the force fields from the element topologies for MD. This novel feature also allows to explicitly differentiate between potential, geometrical and mixed instabilities. Equally, the flexibility and accessibility of the proposed model is enhanced as solely the basic form, $V = V(c)$, of any chosen MD force field and the characteristic variables definitions, $c = c(x, q)$, are needed.

The proposed model can be applied for modelling the effects of defects on the charge distribution in a variety of nanostructures; the piezoelectric property couplings in CNT or PGS during vibrations; $H_2$ storage in PGS; and the effect of probabilistically distributed defects on the fracture initiation, propagation and homogenised properties for different homo- and heteroatomic nanostructures. This ability will allow for the optimised virtual design of nano-based devices for industrial applications such as structural composites, coatings and flexible electronics.

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References


