

A NOVEL ATOMISTIC-CONTINUUM COUPLING METHOD FOR AMORPHOUS POLYMERS AT FINITE TEMPERATURE

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Key words: Concurrent multiscale, Molecular Dynamics, FEM

Abstract. *A new simulation technique, based on the Arlequin framework and the Anchor Point method, is presented for concurrently coupling atomistic and continuum domains at finite temperatures with focus on all-atom molecular representations of thermosetting polymers. The method is derived and then benchmarked using a tensile test on a single graphene sheet. Next, the method is applied to simulate a uniaxial tensile test on a bar of thermosetting polymer (EPON-862 with crosslinking agent DETDA). For the polymer, the first case studied is at a temperature of 1 K in order to reduce thermal oscillation of atoms. Subsequently, results are obtained at 300K, showing large thermally induced oscillations in the system. Work is underway to mitigate this problem.*

1 INTRODUCTION

There are a wide range of problems where localized phenomena in certain regions of the domain are of interest. To be able to study these local phenomena using a high accuracy model, while globally retaining a more efficient, lower accuracy model, has been the subject of research over the past few decades. Research in concurrent coupling seek to partition the domain so that multiple models can operate at the same time. The key to achieving this lies in the interface between the domains and how information is transmitted between their respective models.

In the present work, we seek to address problems in the mechanics of materials and structures. Specifically, our target is to better model nanoscale behaviours in the vicinity of cracks, voids, and nanoparticles in amorphous materials. These nanoscale behaviours can be uncovered using Molecular Dynamics (MD) models within a localized region. Outside of the zone of interest, we may use a continuum model such as the Finite Element Method (FEM). Thus, we have a particle representation of the material in a localized region of interest and a continuum representation elsewhere.

Many of the techniques developed so far for concurrently coupling particle and continuum domains have been specific to crystalline materials. Among the methods designed for amorphous solids, the bridging domain method by Xiao and Belytschko [1] and the Arlequin method by Ben Dhia [2] have been tremendously influential. In this work, we seek to follow in their tracks and the works of others and develop a method with application to all-atom finite temperature modelling of amorphous polymers.

2 METHODS

2.1 Theory

We start our discussion of the theoretical formulation by covering the central ideas of the Arlequin framework in the context of particle-continuum coupling. Subsequently, the concepts of anchor points and interface volume cells are introduced, leading up to the development of the current method. For a more detailed derivation of the Arlequin framework and the anchor point method, the reader is referred to the works by Ben Dhia et al. [3] and Pfaller et al. [4].

The Arlequin method falls in a class of methods, wherein, the particle and continuum domains overlap with each other in a so-called bridging domain. A representative diagram is shown in Figure 1. There are two requirements that must be satisfied in this domain: (i) matching of the particle and continuum displacement fields (and additionally displacement gradient), (ii) a blending of the particle and continuum domain energies. The total energy of the system may be written as a sum of contributions from particle (E_p) and continuum (E_c) domains as follows and needs to be minimized to find the solution:

$$E_{total} = E_p + E_c \quad (1)$$

Both above energies consist of their respective internal energy components and energy due to external sources (tractions and body forces). In order to ensure the particle and continuum energies do not get compounded in the bridging domain, they must be blended, i.e. weighted by a certain factor $\alpha(\mathbf{x})$ and its complement $1-\alpha(\mathbf{x})$ in the respective domains, where \mathbf{x} is the spatial variable.

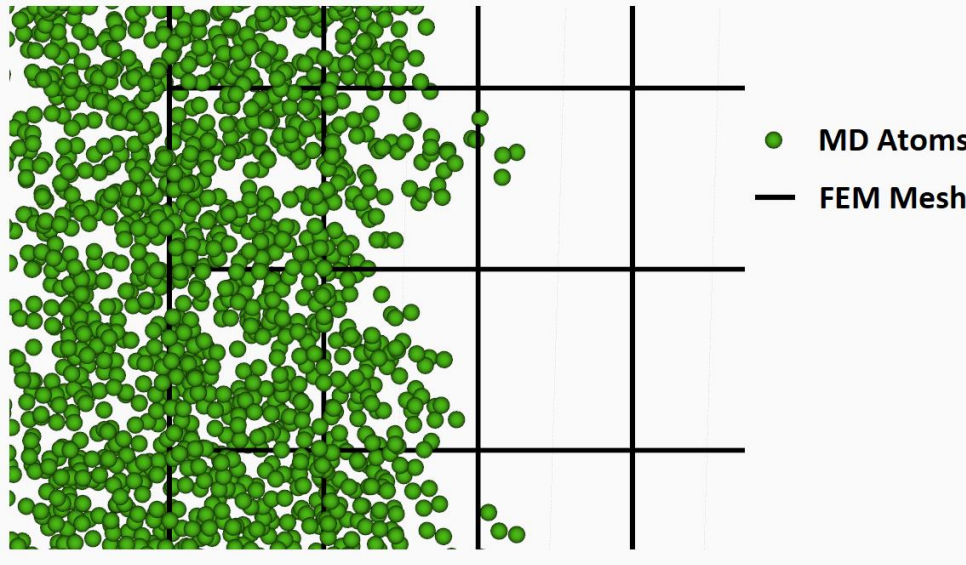


Figure 1: Bridging domain where MD and FEM definitions coexist

In order to satisfy the first requirement of the Arlequin method, i.e. matching the displacement fields in the bridging domain, the problem becomes one of constrained optimization. Using the method of Lagrange multipliers, the Lagrangian for the system is as follows:

$$L = E_p + E_c + \int_{\Omega_b} \boldsymbol{\Lambda} \cdot (\mathbf{U}_c - \mathbf{U}_p) dV \quad (2)$$

In the above equation, $\boldsymbol{\Lambda}$ signifies the Lagrange multiplier field, \mathbf{U}_c and \mathbf{U}_p are the continuum and particle displacement fields respectively, and Ω_b is the bridging domain. It can additionally include a term to account for displacement gradient constraint. In the present work, however, it is not considered.

For cases where the particle domain is represented purely through statics (at 0 K temperature), the solution scheme involves taking the first variations of the Lagrangian with respect to $\boldsymbol{\Lambda}$, \mathbf{U}_c , and \mathbf{U}_p , yielding three systems of equations, which can then be solved to find the saddle point.

Our goal, on the other hand, is to simulate a finite temperature particle domain using molecular dynamics (MD). Pfaller et al. [5] propose staggering the solution into separate particle and continuum steps. In order to do that, a set of dummy particles called anchor points were introduced into the bridging domain, which act as intermediaries to transmit information between the particle and continuum domains. On the particle side, the anchor points transmit forces to the MD particles via springs and on the continuum side, the anchor point displacements can be interpolated into a displacement field which can serve to maintain the displacement field matching constraint. The modified Lagrangian then becomes as follows:

$$L = E_p + E_c + \int_{\Omega_b} \boldsymbol{\Lambda} \cdot (\mathbf{U}_c - \mathbf{U}_{ap}) dV + E_{spring} \quad (3)$$

In the above equation, the field variable \mathbf{U}_p is replaced by \mathbf{U}_{ap} , which is an interpolated anchor point displacement field, and there is an additional energy term as a result of the springs (E_{spring}). While solving for the continuum side, the particle side is held frozen. So, first variations on the Lagrangian do away with the E_p term, generating a system of equations in $\boldsymbol{\Lambda}$, \mathbf{U}_c , and \mathbf{U}_{ap} , solving which, the continuum side energy minimum is found. Next, the calculated anchor point displacements are fed to the particle side, resulting in forces on the MD particles via springs. Holding the anchor points fixed, the MD is moved forward in time. Now, since the spring extensions (and energy) will have changed after the MD run, the continuum side must be solved again. Thus, the two solvers must iterate until some form of convergence is reached.

In their original method, Pfaller et al. associated anchor points with randomly chosen particles in the bridging domain. It must be noted that their particle domain consisted of a coarse-grained representation of a thermoplastic polymer. We, however, seek to use an all-atom representation of a thermosetting polymer, in which case, the matter of choosing which atoms to tether anchor points to is no longer trivial and there is a potential of developing unphysical localized stresses. Thus, we propose a novel extension of the method to circumvent the issue.

We proceed by subdividing the particles lying in the bridging domain into interface volume cells (IVC). The terminology for IVCs is borrowed from the work of Saether et al. [6], wherein they propounded that a successful connection between a discrete atomistic domain and continuum must involve some form of statistical averaging of the atomistic data in both space and time. Each IVC represents a group of adjacent atoms forming a Voronoi cell. By considering the center-of-mass of these cells, averaged over several timesteps in the MD, we may effectively remove the thermal fluctuations and extract displacements that are more

suitable to be fed into the continuum. While the method by Saether et al. coupled these IVCs directly to FEM nodes. We seek to merge with the Anchor Point Method by coupling them in ‘soft’ spring-based manner with anchor points, which in turn inform the continuum displacement field.

2.2 Implementation Details

In this section, we discuss the details of the particle and continuum domains used for testing and the specifics of the concurrent coupling method.

The test material considered in this work was the thermosetting polymer EPON-862 with crosslinking agent DETDA. The particle domain was modelled in an all-atom representation using the OPLS force field [7,8,9] on the software package LAMMPS [10]. In order to create a polymer specimen in MD, a procedure similar to that described in [11] was followed. Firstly, EPON-862 and DETDA molecules in a ratio of 2:1 were randomly distributed inside a 12 x 6 x 6 nm box. The entire system, with periodic boundary conditions, was then allowed to equilibrate at a temperature of 500 K and pressure of 1 atm in an NPT ensemble for 250 ps. At the end of this run, the density of the system reached 0.88 g/cc. At this liquid stage, where crosslinks are yet to be form between molecules, the periodic boundary conditions were removed and molecules at the boundaries were deleted. After deletion, the system consisted of approximately 34,000 atoms. From henceforth in the synthesis, fixed boundary conditions with reflective walls and an NVT ensemble were used. In order to perform crosslinking, the LAMMPS command ‘fix bond/react’ was used which requires the user to specify molecular templates before and after the intended reaction and activates the reaction once two initiator atoms come within a certain radius of each other. For the present work, a bonding radius of 4 Å was used and a procedure similar to [12] was followed. The ‘fix bond/react’ command was periodically activated for a single timestep, followed by 100 ps of equilibration. This was carried on until a crosslinking density of 60% was achieved. The modulus and Poisson’s ratio were calculated for the MD system using a uniaxial tensile test. They are reported in Table 1. A 20 x 20 nm monolayer graphene sheet was also created using the OPLS forcefield.

Table 1: Elastic properties of graphene and polymer calculated from MD

	Modulus (GPa)	Poisson’s Ratio
Graphene	962	0.25
Polymer	3.2	0.4

The continuum domain was modelled using linear elastic FEM with twenty-noded three-dimensional elements. The MD-calculated elastic properties were inputted into the solver.

The concurrent coupling was achieved using the method previously described. Once the FEM mesh is generated, the bridging elements are defined. The Lagrange multiplier field must also be discretized and in the present work, the corresponding mesh exactly overlaps with the bridging domain FEM elements. For simplicity we set each bridging element to be an IVC, though subdivisions of the elements may also be used and will be explored in the future. Once atoms are assigned to IVCs, their initial center-of-mass are calculated by time-averaging over an initial equilibration MD run. The anchor points are instantiated at the initial IVC center-of-mass locations. The anchor field is calculated using the Moving Least Squares method. With

these discretizations in place, the discrete form of the Equation 3, after applying variations, yields linear matrix equation. In each iteration, the matrix equation is solved in the continuum, providing FEM nodal displacements and anchor point displacements. The latter are then fed to the MD where they are tethered to IVC atomic groups by the LAMMPS command ‘fix spring’. Regarding the energy blending, applying a weighting factor to the MD is still a standing problem. As discussed in [13], we may take advantage of the fact that the unphysical non-periodic boundary conditions of the MD will result in a reduction in stiffness towards the boundaries. We thus assume that $\alpha = 0.7$ and apply the factor of $(1-\alpha)$ to the continuum.

3 RESULTS

3.1 Graphene Tensile Test Simulations

We first attempt to benchmark the new method using monolayer graphene, owing to its periodic structure and relative homogeneity. The MD domain is simulated at a temperature of 300 K. The combined FEM and MD domain is shown in Figure 2. The overlap region or bridging domain may be noted. A spring constant of 100 nN/A was chosen for this simulation.

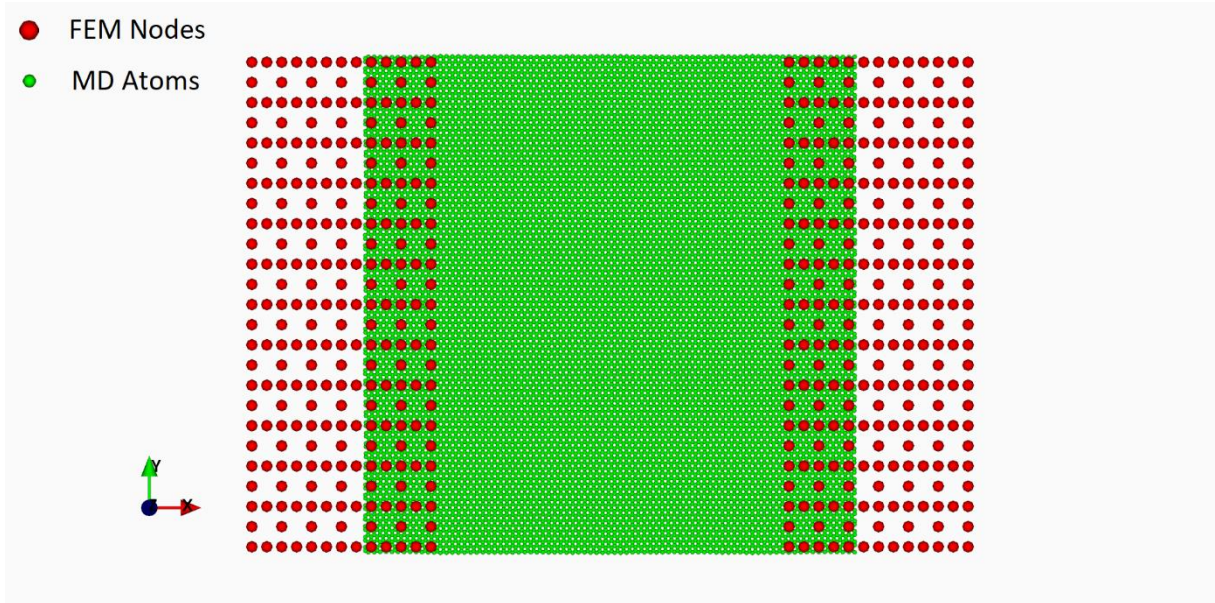


Figure 2: Combined FEM and MD bar-like system for graphene tensile test

A tensile strain of 1% is applied on the FEM domain using displacement control in the X-direction. The convergence of strains in all three domains – pure FEM, bridging, and pure MD – is shown in Figure 3. The FEM strains are calculated as an average of integration point values. The MD strains are calculated from the relative change in IVC center-of-mass positions (which are averaged in time). A similar plot showing the convergence in stresses is shown in Figure 4. The stresses in the MD domain was calculated by averaging per-atom stresses over atoms lying within a 5 x 5 x 5 nm box in the interior of the MD system. The stress in the bridging domain is not straightforward to calculate due to the energy blending and is omitted here. A linear

elastic solution is also shown for comparison based on the elastic modulus inputted into the FEM.

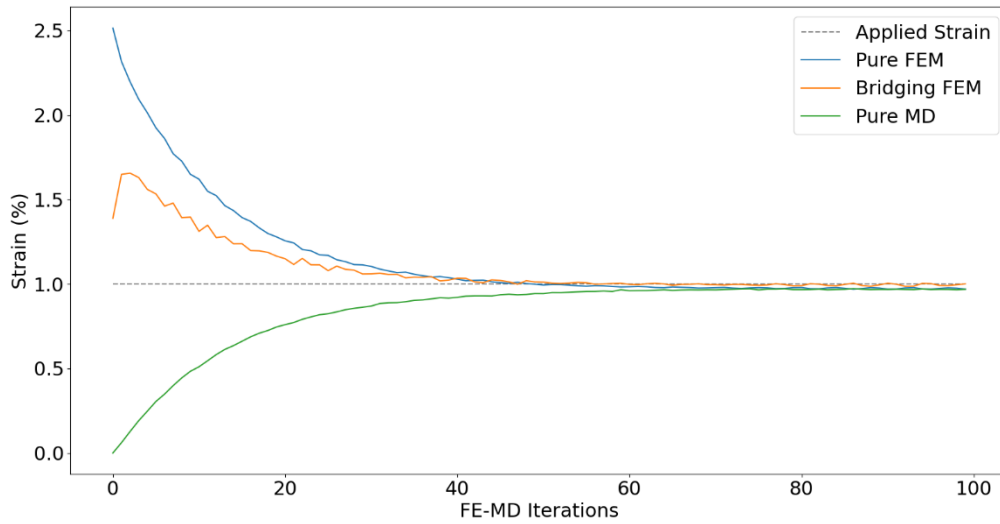


Figure 3: Convergence of average strains ϵ_{xx} in pure FEM, bridging, and pure MD domains with FE-MD iterations layout for graphene tensile test

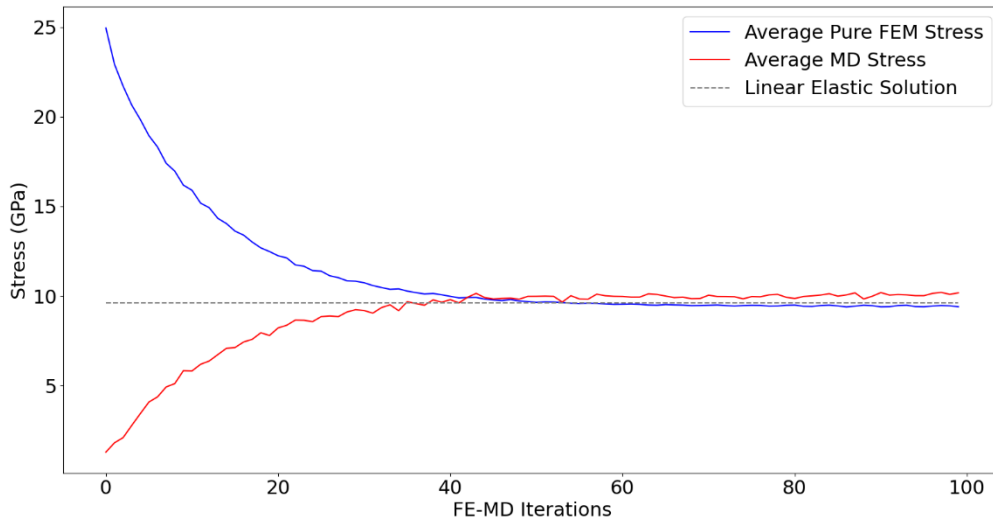


Figure 4: Convergence of average stresses σ_{xx} in pure FEM and pure MD domains with FE-MD iterations layout for graphene tensile test

The final values of strains in the pure FE, pure MD, and bridging domains are reported in Table 2.

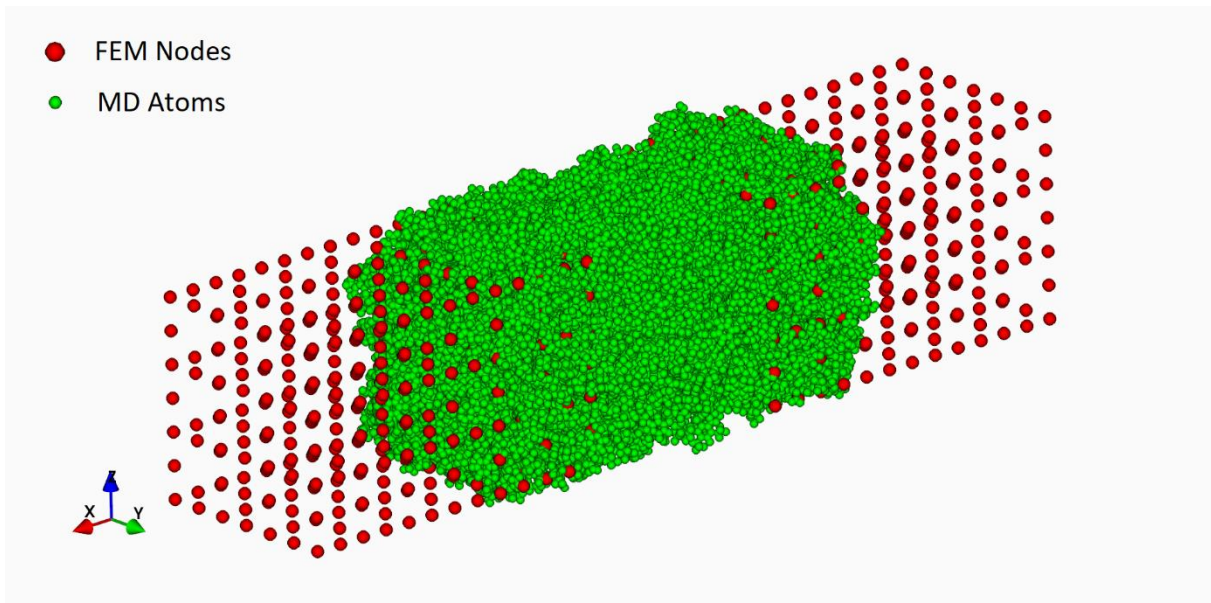
Table 2: Strains in the pure FEM, bridging, and pure MD domains

	ϵ_{xx} (%)	Error in ϵ_{xx} (%)
Applied	1.0	--
Pure FEM	0.975 ± 0.029	-2.467
Bridging FEM	0.989 ± 0.031	-1.064
Pure MD	0.974	-2.646

All three values of strain are very close to the applied strain and the convergence of stresses and strains to steady values serves as a benchmark for our method.

3.2 Polymer Tensile Test Simulations at Low Temperature

Now, to study the validity of the method for all-atom amorphous systems, we first consider a system at 1 K temperature to avoid any thermal fluctuations. The combined FEM and MD system for a tensile specimen of crosslinked EPON-862 is shown in Figure 5. In this case, a spring constant of 0.6 nN/A was used.

**Figure 5:** Combined FEM and MD bar-like system for tensile test

The dimensions of the overall system are 20 x 5 x 5 nm and the MD system is 10 x 5 x 5 nm. A strain of 1% is applied using displacement control on the FEM domain in the X-direction. In Figures 6 and 7, again, the convergence of average strains and stresses are shown in the different domains. It must be noted that during the crosslinking process, it is common for the polymer to develop residual stresses. In the present work, the residual stress in the region of measurement was found to be -41 MPa. The plotted results for MD stress offset this amount in order to start from zero.

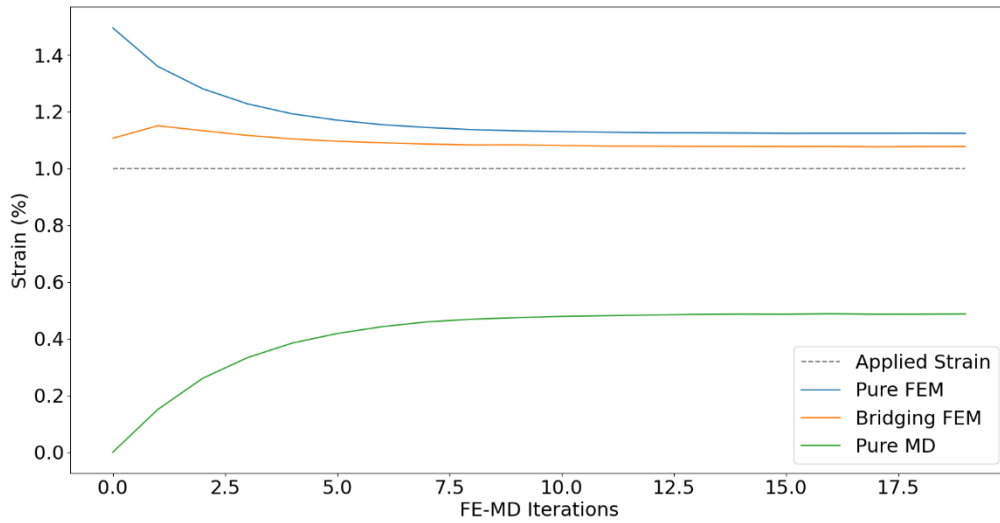


Figure 6: Convergence of average strains ϵ_{xx} in pure FEM, bridging, and pure MD domains with FE-MD iterations layout for EPON-862 tensile test at 1 K

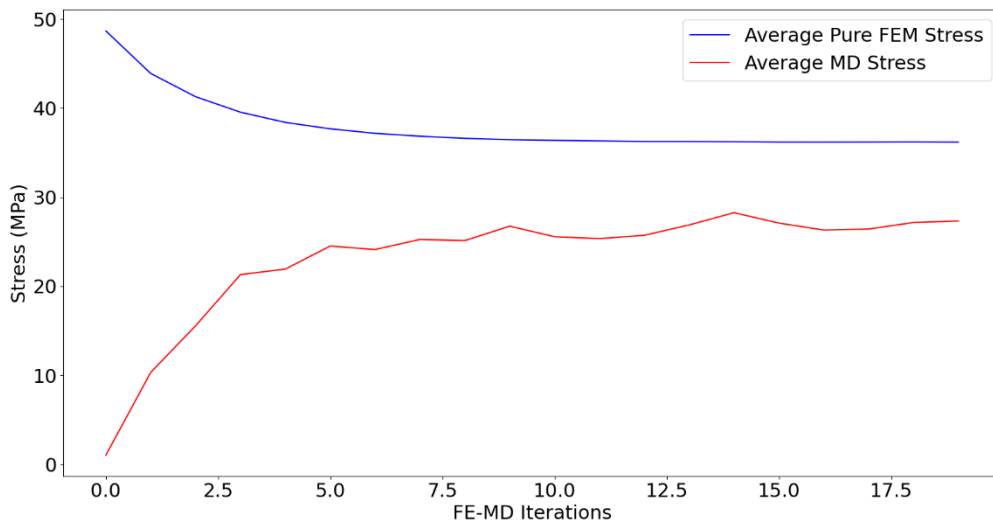


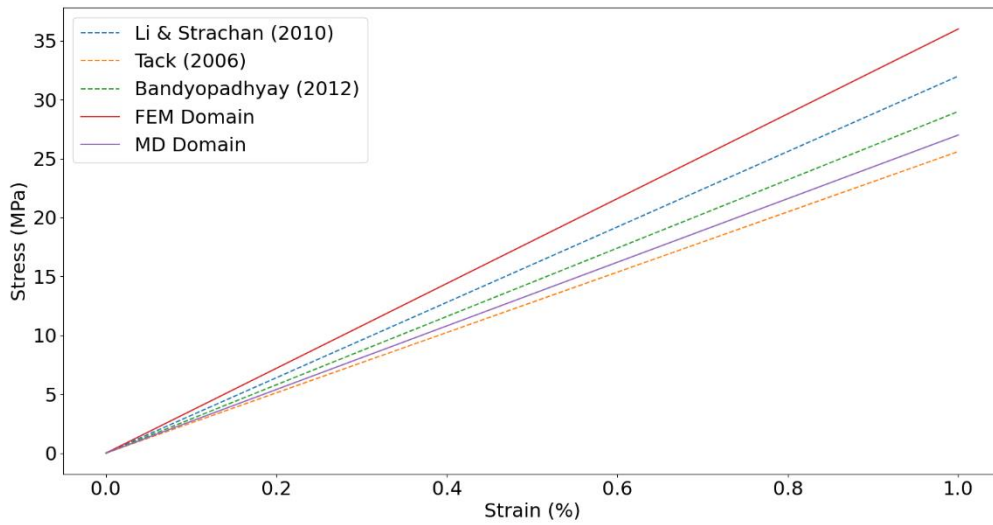
Figure 7: Convergence of average stresses σ_{xx} in pure FEM and pure MD domains with FE-MD iterations layout for EPON-862 tensile test at 1 K

The converged strains are tabulated in Table 3. Convergence occurs much faster at low temperatures. In this case, errors in pure FEM and bridging domain strains are within acceptable limits. However, the MD strain is $\sim 50\%$ lower than the applied. This will require further investigation and exploration of the parameters such as spring stiffness and weighting factor.

Table 3: Strains in the pure FEM, bridging, and pure MD domains

	ϵ_{xx} (%)	Error in ϵ_{xx} (%)
Applied	1.0	--
Pure FEM	1.124 ± 0.046	12.40
Bridging FEM	1.078 ± 0.030	7.775
Pure MD	0.491	-50.9

We also study how the stress-strain plot resulting from our method compares with accepted experimental results [14, 15] and other computational results [12]. Figure 8 shows a comparison of the computed pure FE and pure MD stresses at 1% applied strain with other data.

**Figure 8:** Comparison of stress-strain behavior for pure FEM and pure MD results with other accepted data

All the plotted stresses lie between 25 and 35 MPa. The results from our methods, thus, are comparable with other accepted data.

3.3 Polymer Tensile Test Simulation at 300 K

Finally, we attempt a tensile test for EPON-862 at a temperature of 300 K. The averaged strains and stresses in the different domains are plotted in Figures 9 and 10. The behavior of the MD domain is particularly interesting. While the axial strain is very low, the axial stress is very high. This mismatch likely stems from how strain was being calculated (by the movement of IVC centers-of-mass in the direction of applied strain). Examining the results further we found that there was a high degree of motion in the free Y and Z directions, which is likely causing stresses to form without the end grips having to move.

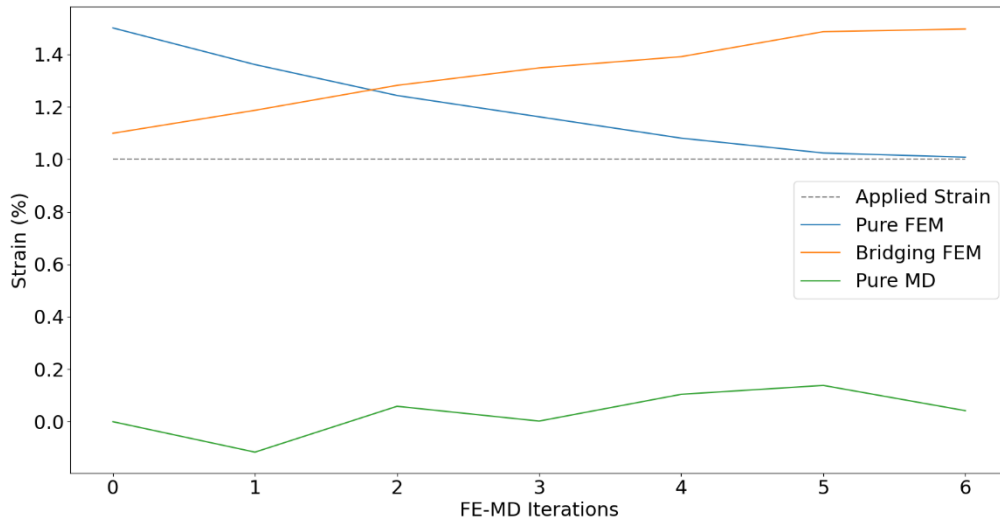


Figure 9: Convergence of average strains ϵ_{xx} in pure FEM, bridging, and pure MD domains with FE-MD iterations layout for EPON-862 tensile test at 300 K

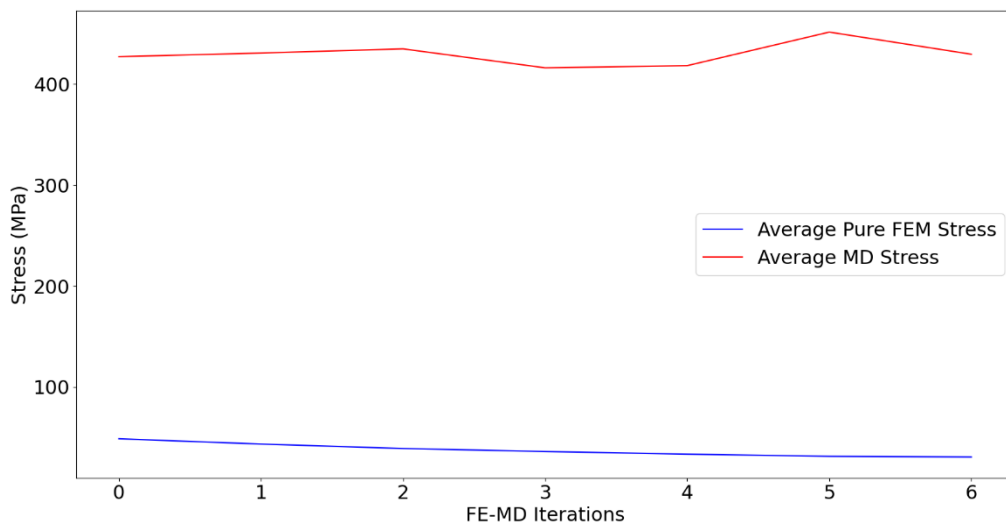


Figure 10: Error in the average strains calculated in the bridging domain FE elements varying with FE-MD iterations layout

It is evident there is strong oscillatory motion being developed due to thermal motion of the atoms in the bridging domain at 300 K. Ultimately, the simulation fails after a certain point due to bonds being stretched beyond allowable limits. These results may be indicative of the need for larger IVC sizes to average out the thermal oscillations before connecting to the continuum

and adjustments to the spring stiffness. This will be the direction of our future work.

4 CONCLUSIONS

- A new method for concurrently coupling a continuum and particle domain was developed for amorphous solids at finite temperature based on the Arlequin method and Anchor Point method.
- The method was successfully benchmarked against a tensile test of monolayer graphene with both strains and stresses in pure FEM, pure MD, and bridging domains reaching an accurate converged value.
- The method was then tested on EPON-862 polymer at a low temperature. The tensile test yielded good results for stresses and strains in the pure FEM and bridging domains. However, the error in the MD domain was significant and requires further investigation and parameter tuning.
- The method was also tested on EPON-862 at a temperature of 300 K. The simulation showed instability and ultimately failed to converge. Future work will attempt to mitigate the issue by adjusting IVC sizes and spring stiffness.

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