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Multiscale Modelling of Aerospace Composites—A Perspective

Parvez Alam
(Institute for Materials and Processes, School of Engineering, University of Edinburgh, UK)

[**Abstract**] This paper introduces a series of approaches in the modelling of composites with complex multiscale structures and features. Fundamental theory underlying multiscale structures are brought to light and discussed. There can be considerable benefit in the representative application of multiscale modelling techniques to civil aircraft design and this aim of this paper is to provide essential perspectives from several fields of research that may be beneficial to aerospace composites modelling methodologies if applied appropriately.
[**Keywords**] molecular modelling; interface modelling; continuum modelling; multiscale modelling

1 Introduction

Aerospace composites are expected to perform under extreme mechanical and environmental conditions, and are often seen as lightweight replacements for metallic materials. Such composites are applied within civil aircraft as engine blades, brackets, propellers, wings and even as interior materials. Traditionally, aircraft parts have been modelled to address issues such as impaction and fatigue, with an aim to elucidate information on service lifetimes and failure behaviour. As such, single scale modelling has been the predominant approach and has given rise to date, to considerable advances in improved design and engineering. Nevertheless, single length scale modelling is not necessarily the most optimal route to analysis since composites and the components they are manufactured into are hierarchically structured at multiple length scales. Furthermore, recent developments in biological composites mechanics has drawn attention to the importance of structural hierarchy to properties such as fracture toughness and strength. Multiscale composites design and manufacture is now receiving significant attention, attracting governmental funding, and enthusing R&D engineers. The current pull towards multiscale materials design clarifies that there is a definitive need to develop standardisation procedures for multiscale materials with respect to testing, manufacture, safety and modelling. The objective of this paper is to provide a perspective as regards the multiscale modelling of composites for use within civil aircraft.

2 Scaling in engineered aerospace composites

Fibre reinforced composites (FRP) are base materials used in the engineering of civil aircraft parts. Traditionally, in the modelling of FRP, the smallest component is usually seen as the fibre, which is typically at the microscale. Yet, fibres are commonly surface treated by coating with polymeric materials (sizing), a process known as surface sizing. Surface sizing has the effect of protecting the fibre from degradation and increasing the compatibility of the fibre (adhesion) to its surrounding matrix, which will itself be a thermosetting or thermoplastic polymer. Surface sizing glass fibres commonly entails coating with silane-based polymers, whereas for carbon fibres, epoxies, phenolics or esters are more commonly used. The sizing itself is nevertheless, a molecular to nanoscale composite component and as such, its treatment within a model

system is best not ignored. The sizing will not only change the topography of the fibre (varying thus the strength of interlocking between fibre and matrix), but will also increase the specific surface area (SSA), which in turn increases the number of secondary adhesive interaction sites between the fibre surface and the matrix material. These aspects at the molecular to nanoscales will affect the energy required to debond fibre and matrix, which affects the overall strength and fracture energy of the composite at its macroscale. A macroscale model thence, that does not incorporate the effect of molecular to nanoscale interactions at fibre-matrix interfaces, will be inherently flawed in its ability to predict strength and fracture. Multiscale modelling for an FRP is therefore a means by which interface phenomena can be more accurately represented and thus, incorporated within a macroscale model, circumventing thus, the need for correction factors applied to interface definitions, or indeed to entire models, for the sake of fitting.

As a result of extensive increases in computational power, improvements to parallelisation tools and developments in graphics processing unit (GPU) technologies, larger model systems can be simulated with greater relative ease. This has empowered molecular dynamics modelling and coarse grain modelling in a way that allows users to simulate massive clusters of atomistic systems, sometimes reaching up to hundreds of millions of atoms within one single model. As such, molecular to nanoscale sizing interactions with fibre surfaces and with matrix materials can currently be simulated fairly easily. Furthermore, detail from such simulations, such as interaction energies, can be incorporated into larger (macro) scale finite element models at interfaces to more accurately predict the global mechanical properties of FRP. Subsequent sections in this manuscript will detail basic theory in molecular to nanoscale modelling.

3 Atomic interactions

Atom-atom interface interactions and the way in which they are defined are essentially the cornerstones for atomistic modelling. Two predominating philosophies are routinely incorporated into atomistic modelling software. These include empirical as well as quantum mechanical representations. Both representations are currently indispensable in the more prominent atomistic modelling methods including Monte Carlo, Molecular Dynamics and the Lattice Energy Methods.

Empirical representations are borne essentially, from currently accepted empirical equations that have been derived to describe atomic separation. A benefit of this approach to the atom-atom interface is that it can be easily modified to the parameters of a specific equation. A classical example of an empirical model that is still used in simulations concerning certain ionic materials is the long range Coulomb Interaction Model with short range repulsion, Equation (1)[1]. Here, E is energy, r is the atom-atom spacing, L and η are correction factors that correspond to the empirical data set. An alternative, simpler model has greater functionality in that, unlike the Coulomb Interaction Model, harmonic functions such as torque and bond angle can be easily incorporated, Equation (2).

$$E(r) = Le^{(-r/\eta)} \quad (1)$$

$$E = Lx^{\eta} \quad (2)$$

Quantum mechanical models are different and are essentially probabilistic models. They have no reliance on empirical data and have no need for correction factors or simulation specific modifications to constitutive interatomic relations. Quantum mechanical models yield reliable simulation results and have particular benefit in *ab initio* simulations where electrostatic optimisations of complex molecules may be necessary. Being a probabilistic approach, quantum mechanical models also have the added benefit of predicting the charge sharing effect of any deviation of a molecule, thus allowing for subtle variations in chirality, and isomerism to be modelled and compared with relative ease. In the quantum mechanical approach, electrons travel within electrical fields created by nuclei. The coinciding wave functions, Ψ, are shared between existing nuclear, vibrational, rotational and electronic wave functions.

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$$\Psi = \Psi_{\text{electronic}} + \Psi_{\text{vibrational}} + \Psi_{\text{rotational}} + \Psi_{\text{nuclear}} \quad (3)$$

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{nuclear}} \quad (4)$$

An alternative to using wave functions in the quantum mechanical methods is DFT (density functional theory)[2]. The fundamental difference between the two methods here is that DFT employs electron densities in the determination of interatomic activity. DFT uses the approximation shown in Equation (5), in which energy is a summation of both kinetic and potential energies. Here, U_k is the kinetic energy, $U_{p\text{-}e}$ is the potential energy of electrons arising through repulsion and $U_{n\text{-}e}$ is the potential energy of atomic electrons arising through attraction to the nucleus, which is positively charged.

$$E = U_k + U_{p-e} + U_{n-e} \quad (5)$$

4 Molecular interactions

Molecules are typically modelled from the atomistic principles previously described. When considering *molecular interfaces*, there is a need to contextualise the specific interface under scrutiny. Considerable efforts have been made in this respect within the biological sciences. Molecular modelling methods such as MD and MC can be useful for modelling e. g. molecular folding mechanisms and intermolecular interactions. However, when modelling very large sets of molecules containing millions, perhaps billions of atoms, the need for structural and interfacial approximations becomes apparent. There are a few important articles that can be cited as useful templates to dealing with these inherently complex systems.

One such article[3] uses probabilistic functions in the form of Bayesian networks to distinguish interfacial characteristics between interacting molecules. The Bayesian network is very useful since it is essentially a steered probabilistic method representing variables and their conditional dependencies through a directed non-cyclic graph. The strength of the method is in its simplicity. Dependent variable outputs are either *true* or *false*, allowing thus for the incorporation of numerous variables with relative ease. The Bayes hierarchical Bayesian network can most simplistically be written,

$$p(a, b|x) \propto p(x|a)p(a|b)p(b) \quad (6)$$

Here, a is a prior originating from the prior probability $p(a)$ of the fundamental Bayesian form $p(a|x) \propto p(x|a)p(a)$. The prior a depends on parameter b all of which relate to x data. A likelihood, $p(a|b)$, and a new prior, $p(b)$, replaces the prior probability, $p(a)$ for the hierarchical form in Equation (6). Bradford and co-workers[3] distinguish between interacting and non-interacting patches at molecular interfaces by five variables. These are shown in Figure 1.

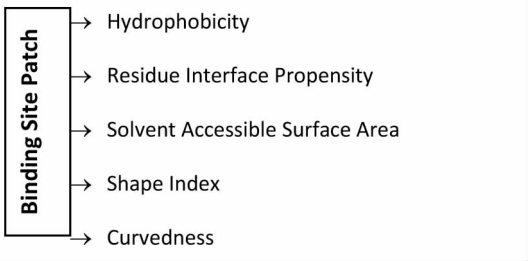

Figure 1 Bayesian parameters employed by Bradford et al. (2006) for intermolecular interactions.

Jones and Thornton (1997)[4] consider a different approach to studying intermolecular interaction sites. They worked from a basis of molecular interfaces being hydrophobic[5-6], using proteins as examples. They studied essentially the same variables shown in Figure 1, but in discrete *patches* defined by a finite number of residues. A similar patch by patch method used by Preissner et al. (1998)[7] suggests that approximations based on molecular structure can be made for larger scale simulations. For low density systems simulations of structures are might employ Monte Carlo based approximations, Equation (7), such as have been used with LAMPPS open source software. This is a probabilistic (statistical) approach to approximating interface properties. In the equation, we have N configuration, of a system with ξ_1, ξ_2, ξ_3, $\xi_4 \cdots \xi_P$ where $P(\xi)$ is a given probability distribution.

$$\lim_{N\to\infty} \frac{N_\xi}{N} = P(\xi) \quad (7)$$

A bisector method developed by Seong et al. (2011)[8] has potential for speeding up molecular cluster interface interaction predictions. This method can take essentially, large clusters of atoms and bisect

between them to form a plane traversing through Euclidean space yet connecting solely the intersecting points. The bisector exists in a real time environment and as a consequence, a great variety of computations can easily be applied with very little cost in memory.

5 Nanomechanics

When surface structures are nano-scale, they will exhibit dimensions below 100nm in at least one direction. Recent work has shown that nanocrystals in contact with soft amorphous phases give rise to semi-crystalline metastable states that can take both amorphous and crystalline forms depending on the loading conditions[9-10]. In hierarchical modelling, there may be a need to transition from the molecular to nano, or even micron scales. Typically higher scale models will lack atomistic detail. Yet details in low to high scale transitions, and in the better case scenario, specific properties should be incorporated for more appropriate model predictions. One example is the nano-effect. The nano effect can best be described as relating to the balance between bulk and free surface properties. At the molecular level surface/molecular energies dominate, whereas at the macro scale, the properties of a body of matter are determined by the energy of the bulk. Surface and bulk properties are considerably different and at the nano-scale, as a function of atomic volume, the surfaces contribute considerably to the overall properties of the nanomaterial and cannot be neglected.

We may begin by considering a nano-object as consisting of two phases, a bulk, α, and a surface, β[11]. Energetically, these can be considered to exist in a state of continuum with an interface separating each phase. The elastic surface energy[12] between the two phases, U_s, can be represented by Equation (8).

$$U_s = U - (U_\alpha + U_\beta) \tag{8}$$

Here U is the internal energy of the system and $(U_\alpha + U_\beta)$ is the total uniform energy in both parts. Notably, $(U_\alpha + U_\beta)$ can be modified to include any variations in energy at the surface. It should be noted that the surface is in a continual state of (molecular) motion. When the nanostructure surface dominates the bulk, this motion can be considerable and *work energy* at the surface needs to be accounted for. This can be defined according to Equation (9).

$$W_s = \gamma dA \tag{9}$$

Here, A is the area of the surface and γ is the surface stress. Surface deformation of a compressible material induces a volumetric, V, change in each phase such that:

$$dV_\alpha = -dV_\beta \tag{10}$$

The general surface deformation can be expressed as a strain, ε_s:

$$\varepsilon_s = dA/A \tag{11}$$

and the surface stress is approximated from Shuttleworth (1950)[13]:

$$\gamma = \mathrm{E}_s + \partial \mathrm{E}_s/\partial\varepsilon_s \tag{12}$$

where E_s is the free energy of the surface. Different approximations for the surface stress can be made following[14] as:

$$\gamma = \mathrm{E}_s + \partial \mathrm{Es}/\partial\varepsilon_e \tag{13}$$

which can alternatively be expressed:

$$-\partial \mathrm{E}_s/\partial \mathrm{E} = q + (\mathrm{E}_s - \gamma)\,\partial\varepsilon_e/\partial \mathrm{E} \tag{14}$$

where ε_e is the elastic surface deformation, E is the electrode potential and q is the surface charge density. With respect to the above equations, it is well worth noting that to date, none have yet been proven experimentally[15]. Numerous flaws can be brought to light in both the Shuttleworth and the Couchman forms. Marichev suggests that since the 1st and 2nd Gokhstein equations have been confirmed experimentally, (see [16-17]) that they rather be used as determinants of surface tension for solid materials.

$$(\partial\gamma/\partial q)_\varepsilon = (\partial E/\partial\varepsilon_e)_Q \quad -1^{\mathrm{st}}\ \text{Gokhstein eq.} \tag{15}$$

where Q is the surface charge.

$$-\partial\gamma/\partial q = q + \partial q/\partial\varepsilon_e \quad -2^{\mathrm{nd}}\ \text{Gokhstein eq.} \tag{16}$$

In a nanomaterial both phases α and β can be considered solids. It follows then, that when the surface of α strains, work is done at the interface between α and β. During deformation, the total work for a *solid-solid interface*, W_{s-s}, combines three separate work terms.

$$W_{s-s} = E_{s-s}(dA_{s-s}) + \gamma_{s-s}(dA_\alpha) + \gamma_{s-s}(dA_\beta) \tag{17}$$

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where the term $E_{s-s}(dA_{s-s})$ is the work required to create a new surface, $\gamma_{s-s}(dA_\alpha)$ is the work required to deform phase α about the interface and $\gamma_{s-s}(dA_\beta)$ is the work required to deform phase β about the interface the same extent as α. E_{s-s} is the interface energy, γ_{s-s} is the interface stress, A_{s-s} is the interface area and A_α and A_β are the areas related to deformation in α and β solids respectively. Though total work also exists in micro and macro scale materials with interfaces, because the bulk phase dominates dimensionally and with regards to properties, the total work term at a nanointerface can effectively be reduced to:

$$W_{s-s} = E_{s-s}(dA_{s-s}) \tag{18}$$

This simplification is possible because $\{\gamma_{s-s}(dA_\alpha) + \gamma_{s-s}(dA_\beta)\}$ is negligible and the magnitude of $\{\gamma_{s-s}(dA_\alpha) + \gamma_{s-s}(dA_\beta)\}$ relative to $\{E_{s-s}(dA_{s-s})\}$ heightens as the dimensions of each phase comes closer to the nanoscale. Thus, both surface and interfacial effects described here cannot be ignored at the nanoscale. Indeed, surface dominating characteristics at the nanoscale may well be a cause for mechanically beneficial phenomena such as molecular pinning[18].

The total mechanical work in a composite material, W_c, is a summation of the work done in the bulk material of phases α and β, W_α and W_β respectively with the work done at the solid-solid interfaces. In much larger-than-nanoscale materials,

$$(W_\alpha + W_\beta) >> W_{s-s} \tag{19}$$

$$\text{and therefore } W_c \rightarrow (W_\alpha + W_\beta) \tag{20}$$

while in nanostructured materials,

$$(W_\alpha + W_\beta) << W_{s-s} \tag{21}$$

$$\text{thus } W_c \rightarrow W_{s-s} \tag{22}$$

6 Interfaces at higher length scales

At the nanoscale, tractive forces may still be modelled as molecular sliding. However, as we increase the length scale, molecular models turn out to be impractical in many ways. There is an increased (perhaps unnecessarily so) CPU/GPU demand alongside memory consumption. There is also more data that requires considerable effort to analyse. Finally there is the unfortunate, but often experienced scenario of long run-time models that turn out to have been developed incorrectly. The predominating question would be: is there any added benefit of scaling an atomistic model up with more atoms, or can we reach the same conclusions and interpretations from our model by making use of more appropriate modelling methods for higher scale materials? The author of this manuscript considers that observed incoherency between length-scales may in fact be a function of inadequately or indeed inaccurately described interfaces. In this section we describe some simple means by which larger scale structural models can be made more representative of hierarchical composites.

Energy transfer and interfacial motion havs already to some extent been covered in the previous section on nanomechanics. Nevertheless above the nanoscale, work energy at the interface takes the full form of Equation (17) with no further simplification. This energy is holistic in that, the deformation that gives rise to it may be one or a combination of a multitude of forms. These may include typically friction, viscoelastic or viscoplastic resistance, crack resistance and topographical interlocking. It is worth mentioning that each characteristic is essentially a function of molecular level behaviour. Thus, appropriate approximations must be made when applying molecular mechanical computations to macro-scale interface properties. There are a number of ground level relationships that are already in use that can be manipulated to semi-empirical forms or from basis molecular computations.

We can start simply by considering mechanical energy transfer across a boundary. Assuming molecular level computations are correct, that a boundary system is in continuum, and that the energy scalar follows from the previous boundary, we can easily return to Equation (17), which accounts for the three phases of α, β and interface. One important issue to address in regards to Equation (17) is that the *effects from specific* interface characteristics need to be included for the form to function more realistically in transition from molecular modelling to macro-scale (e. g. finite ele-

ment) modelling. When friction is the dominant mode of irrecoverable interfacial deformation, changes to this general understanding of deformational work are to be modified. Energy will be lost when molecules slide and the term $E_s - s(dA_{s-s})$ requires thus, modification to account for non-linear reductions in work energy as a function of the initial transition from stored work energy to molecular sliding, f_s, and subsequent kinetic friction, f_d, where molecules are in continuous sliding motion. In such a case therefore,

$$E_{s-s}(dA_{s-s}) = f(f_s N, f_d N) \quad (23)$$

Where N is the normal force acting between phases α and β. This approximation has numerous limitations including; an assumption that the normal force and frictional force are linearly proportional, that the contacting area is not in a state of *atomic saturation* (i. e atom-atom contact is not in continuum), and that theoretical materials can follow what is essentially an empirical construction. The great versatility of this model however is its simplicity and it is thanks to the simplicity that it can be modified via semi-empirical or theoretical corrections.

Such corrections can be tuned to the *material properties* of the interface. Keeping the assumption that normal and frictional forces are proportional, alternative force approximations related to e. g. viscoelasticity can be made. The important point here is that the variable N can be manipulated relatively painlessly in series form to establish (in the case of viscoelasticity) the force per unit time as a function of the strain rate. The series may be applied from an empirically determined (or indeed computationally determined) data sets, or from a direct mathematical function, such as in a Prony series.

Defining an interface with material properties *and* fractal topographical irregularity is somewhat more challenging and requires consideration of the local deformational characteristics of individual protuberances, the way by which the protuberance affects force transfer and interface motion, and the subsequent non-linear variations as a function of protuberance shape. Discretisation is of course the normal route to dealing with complex geometry. This said; fractal surfaces are problematic in that they will reach a dimension that can no longer be rendered and interpolation functions should be rather used to define fractal induced behaviour. Good derivations of such functions can be found in Mistakdis and Panagouli (2003)[19]. In short, the *fractal effect* increases friction at lower orders but as the fractal order increases, its effects on friction becomes less obvious than its preceding orders.

7 Conclusions

In this paper, we briefly highlight the importance of interface considerations in the hierarchical modelling of composites. We consider the fundamentals of interface modelling from the atomistic level, through the molecular and the nano levels, and finish at the macro level of modelling. The understanding and application of justifiable interface conditions at every length scale is critical to the development of stable, fast working, effective, yet accurate models.

References

[1] Born M, Mayer JE. 1932. Zur Gittertheorie der Ionenkristalle. Zeitschrift für Physik, 75:1 – 18.

[2] Payne MC, Teter MP, Allan DC, Arias TA, Joannopoulos JD. 1992. Iterative minimization techniques for ab initio total-energy calculations-molecular dynamics and conjugate gradients. Reviews of Modern Physics, 64:1045 – 1097.

[3] Bradford JR, Needham CJ, Bulpitt AJ, Westhead DR. 2006. Insights into protein-protein interfaces using a Bayesian network prediction method. Journal of Molecular Biology, 362: 365 – 386.

[4] Jones S, Thornton JM. 1997. Analysis of protein-protein interaction sites using surface patches. Journal of Molecular Biology, 272:121 – 132.

[5] Korn AP, Burnett RM. 1991. Distribution and complimentarity of hydropathy in multisubunit proteins. Proteins: Structure, Function, Genetics, 9:37 – 55.

[6] Young L, Jernigan RL, Covell DG. 1994. A role for surface hydrophobicity in protein-protein recognition. Protein Science, 3:77 – 729.

[7] Preissner R, Goede A, Fr? mmel C. 1998. Dictionary of interfaces in proteins (DIP) data bank of complementary molecular surfaces patches. Journal of Molecular Biology, 280: 535

2017年第3期 总126期
ISSN 1674-9804 CN 31-1614/V

-550.

[8] Seong JK, Baek N, Kim KJ. 2011. Real-time approximation of molecular interaction interfaces based on hierarchical space decomposition. Computer-Aided Design, 43: 1598-1605.

[9] Sintya E, Alam P (2016a). Self-assembled semi-crystallinity at parallel-beta sheet nanocrystal interfaces in clustered MaSp1 (spider silk) proteins. Materials Science and Engineering C, 58:366-371.

[10] Sintya E, Alam P (2016b). Localised semi-crystalline phases of MaSp1 proteins show high sensitivity to overshearing in beta-sheet nanocrystals. International Journal of Biological Macromolecules, 92:1006-1011.

[11] Alam P. 2015. Mechanical properties of bio-nanostructured materials. In: Handbook of Mechanical Nanostructuring, pp. 211-231, Wiley-VCH, ISBN 978-3—527-33506-0.

[12] Gibbs JW. 1961. On the equilibrium of heterogeneous substances. In: The Scientific Papers of J. Willard Gibbs, Volume 1: Thermodynamics, New York, Dover, 55-353.

[13] Shuttleworth R. 1950. The surface tension of solids. Proceedings of the Physical Society. Section A, 63(5):444.457.

[14] Couchman PR, Davidson CR. 1977. The lippmann relation and surface thermodynamics. Journal of Electroanalytical Chemistry, 85(1-2):407-409.

[15] Marichev VA. 2011. The Shuttleworth equation: is modifications and current state. Protection of Metals and Physical Chemistry of Surfaces, 47(1):25-30.

[16] Gokhshtein, AY. 1970. Investigation of surface tension of solid electrodes at several frequencies simultaneously. Electrochimica Acta, 15(1):219-223.

[17] Gokhshtein AY. 1975. The estance method. Russian Chemical Reviews, 44(11):921-932.

[18] Touaiti F, Alam P, Toivakka M, Bousfield DW. 2010. Polymer chain pinning at interfaces in $CaCO_3$-SBR latex composites, Materials Science and Engineering A, 527: 2363-2369.

[19] Mistakidis ES, Panagouli OK. 2003. Friction evolution as a result of roughness in fractal interfaces. Emgineering Computations, 20:40-57.