MICROMECHANICS-BASED PREDICTION OF THERMOELASTIC PROPERTIES OF HIGH ENERGY MATERIALS

by

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ABSTRACT

High energy materials are used as propellants in solid rockets. Multiscale simulations of these materials require techniques that can bridge submicron scales and engineering scales. Micromechanics provides such techniques. The objective of this research is to investigate micromechanics approaches that can be used estimate the effective thermoelastic properties of high energy materials given the properties of the components.

In this research, rigorous bounds and analytical estimates for effective elastic properties are reviewed and applied to mock polymer bonded explosives and the explosive PBX 9501. A method of estimating three-dimensional elastic properties from two-dimensional finite element simulations is presented. Since detailed numerical simulations of PBXs are computationally expensive, two computationally inexpensive techniques are explored: the generalized method of cells and a renormalization-based approach called the recursive cell method.

Results show that rigorous bounds and analytical approximations provide inaccurate estimates of the elastic properties but reasonable estimates of the thermal expansion of PBX 9501. Finite element simulations of glass-estane composites overestimate the elastic moduli unless particle-binder debonding is included. Results for models of PBX 9501 show that the particle distribution, mesh discretization, and stress-bridging affect the estimated properties considerably. The generalized method of cells is shown to underestimate the elastic moduli because of inadequate consideration of stress-bridging and shear-normal coupling. The renormalization-based recursive cell method overestimates the effective properties unless large blocks of subcells are renormalized. Comparisons with exact relations provide useful checks of the accuracy of numerical methods. Detailed numerical simulations appear to be required for the accurate prediction of elastic properties of polymer bonded explosives.
To Champa
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CHAPTER 1
INTRODUCTION

For many years, scientists have felt the need to predict the behavior of materials from atomistic scales to engineering scales. The recent advent of massively parallel computers and improved simulation techniques have made that goal realistic. Multiscale simulations are usually performed in one of two ways. In the first approach, material behavior is simulated by detailed models at a lower scale and then “coarse grained” so that this information can be used at a larger scale. The computational approaches can be independent of each other at each scale in this approach. The second approach attempts to link the scales by allowing some interaction between models at different scales. Micromechanics provides a means of “coarse-graining” information from submicron simulations to engineering scales and can be used in either approach.

High-energy (HE) materials are commonly used as propellants for solid rocket motors. Interest in the mechanical properties of HE materials has developed with improvements in computational capabilities that make possible simulations of containers filled with these materials. Though mechanical properties of HE materials can be determined experimentally, the hazards associated with experiments on these materials, as well as the attending costs, make this option unattractive. Improved numerical and computational techniques make the determination of mechanical properties of HE materials possible by bridging the gaps between atomistic calculations of molecular potentials, molecular dynamics simulations and micromechanics methods for composite materials. In this research, some micromechanics-based methods for the determination of the mechanical properties of composites are explored and applied to a group of HE materials called polymer-bonded explosives (PBXs).

PBXs provide unique challenges for micromechanical modeling. These materials
are viscoelastic particulate composites, contain high volume fractions of particles, and
the modulus contrast between the particles and the binder is extremely high. For ex-
ample, PBX 9501 contains about 92% by volume of particles and the modulus contrast
between particles and the binder, at room temperature and low strain rates, is around
20,000. Micromechanics predictions based on analytical approximations are inaccurate
because of the high modulus contrast and volume fraction of PBXs. On the other hand,
micromechanics predictions from numerical simulations require extremely large grids to
accurately capture the microstructure of PBXs.

To reduce the complexity of the problem, some simplifying assumptions are made
about PBXs in this research. It is assumed that PBXs are two-component particulate
composites with the particles surrounded by a binder. The components of PBXs are
assumed to be isotropic and linear elastic, and only the prediction of elastic moduli and
coefficients of thermal expansion (CTEs) of PBXs is addressed. Simplified numerical
techniques such as the generalized method of cells (GMC) and the recursive cell method
(RCM) are explored as alternatives to direct simulations using the finite element method
(FEM). The finite element method (FEM) has been used to provide benchmark calcula-
tions of effective properties of PBXs.

1.1 Outline of the dissertation

A review of the properties of polymer bonded explosives and PBX 9501 is provided
in Chapter 2. Rigorous bounds on the effective properties of composites are discussed
next and applied to predict the properties of PBX 9501. Some analytical approaches are
also reviewed and applied to PBX 9501. A discussion of various numerical microme-
chanics methods of predicting the effective properties of composites is provided.

Chapter 3 deals with the estimation of effective elastic properties of glass-estane
mock propellants. The mock material has been chosen because the low volume fraction
of glass beads and the monodisperse nature of the beads eliminate two of the variables
of concern: high particle volume fractions and different particle sizes. Bounds and
numerical estimates using the finite element method for the effective elastic moduli
of these composites are obtained and compared to experimental data. The effect of
the size of the unit cell used in finite element simulations is investigated. Effective properties predicted by two- and three-dimensional finite element models are compared. In addition, the effect of particle-binder debonding on the effective properties of these composites is explored.

In Chapter 4, two-dimensional finite element analyses are used to predict the effective properties of high volume fraction polymer bonded explosives such as PBX 9501. The approach is validated by way of comparisons with differential effective medium estimates of Young’s modulus and predictions from three-dimensional finite element models. Various microstructures based on the particle size distribution of PBX 9501 are modeled using two-dimensional finite element analysis and the predicted properties are compared with experimental data.

A computationally inexpensive alternative to direct finite element simulation for some composites is the generalized method of cells (GMC). Chapter 5 discusses the formulation of GMC and its applicability to polymer bonded explosives. Estimates of effective properties of polymer bonded explosives from GMC are compared to finite element based estimates and experimental values. The issue of stress-bridging due to contact between particles is also explored in the context of GMC.

Chapter 6 deals with a real-space renormalization group method for determining the effective properties of composites called the recursive cell method (RCM). Predictions of effective properties from this method for a range of volume fractions and modulus contrasts are compared to estimates from finite element calculations. Estimates of effective elastic properties of models of polymer bonded explosives from the RCM technique are then compared to those from finite element analyses. The RCM technique is also used to explore the percolation behavior of high modulus contrast particulate composites.

Finally, some exact relations for the determination of effective properties of composites are discussed in Chapter 7. The predicted effective properties from these exact relations are compared with estimates from finite element calculations, the recursive cell method, and the generalized method of cells. The usefulness of exact relations in determining the accuracy of the three numerical techniques is discussed in the context of high modulus contrast particulate composites.
CHAPTER 2

BACKGROUND

2.1 Polymer-bonded explosives

Polymer-bonded explosives (PBXs) are particulate composites containing two or more components. One of the components is an explosive crystal while the other components act as a binder that provides structural support to the crystals. Some PBXs and their components [1, 2, 3] are listed in Table 2.1. It can be observed from the table that all these PBXs contain a very high weight fraction of particles (> 90%). In most cases, at and above room temperature, the particles are considerably stiffer than the binder.

2.1.1 PBX 9501

The polymer-bonded explosive of interest in this research is PBX 9501 because of the availability of experimental data on the mechanical behavior of this material. PBX 9501 is a particulate composite containing crystals of HMX (High Melting Explosive) in a binder composed of Estane 5703 and BDNPA/F. In addition, a free radical inhibitor such as diphenylamine or Irgonox is usually added to the binder [4]. A detailed composition of PBX 9501 is shown in Table 2.2. The small volume fraction occupied by Irgonox can be neglected. The voids occupy only 2% of the volume and are neglected in this research.

2.1.1.1 Elastic properties of PBX 9501

The elastic moduli of polymer bonded explosives are strongly influenced by strain rate and temperature [7] because of the strain rate and temperature dependent behavior of the binder. In general, the compressive strengths and elastic modulus of polymer-bonded explosives increase with decreasing temperature and increasing strain rate. The above observations are also true for PBX 9501.

Temperature and strain rate dependent moduli of PBX 9501 reported by Wetzel [8] and obtained from experiments performed by Wiegand [9], Dick et al. [5], and Gray et
Table 2.1. Compositions of common PBX materials.

<table>
<thead>
<tr>
<th>Binder Type</th>
<th>PBX</th>
<th>Explosive/Binder</th>
<th>Weight (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoropolymer</td>
<td>LX-10-1</td>
<td>HMX/Viton</td>
<td>95.5/4.5</td>
<td>[1]</td>
</tr>
<tr>
<td>(e.g., Viton)</td>
<td>PBX 9502</td>
<td>TATB/KEL-F-800</td>
<td>95/5</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>PBX 9010</td>
<td>RDX/KEL-F-3700</td>
<td>90/10</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>PBX 9407</td>
<td>RDX/Exon-461</td>
<td>94/6</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>PBX 9207</td>
<td>HMX/Exon-461</td>
<td>92/8</td>
<td>[2]</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>PBX 9011</td>
<td>HMX/Estane 5703</td>
<td>90/10</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>EDC 29</td>
<td>HMX/HTPB</td>
<td>95/5</td>
<td>[3]</td>
</tr>
<tr>
<td>Polyurethane (with plasticizers)</td>
<td>PBX 9404</td>
<td>HMX/NC+CEF(1:1)</td>
<td>94/6</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>EDC 37</td>
<td>HMX/NC+K10(1:8)</td>
<td>91/9</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>PBX 9501</td>
<td>HMX/BDNPA/F(1:1)</td>
<td>95/5</td>
<td>[2]</td>
</tr>
</tbody>
</table>

a HMX : 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
b Viton : random copolymer of hexfluoropropane and vinylidene fluoride (1:2)
c TATB : triaminotrinitrobenzene
d KEL-F-800 : random copolymer of chlorotrifluoroethylene and vinylidene fluoride (3:1)
e RDX : C3 H6 N6 O6
f KEL-F-3700 : (CFClCF2CH2CF2)n
g Exon-461 : (CFClCF2CH2CF2)n
h Estane 5703 : segmented polyurethene of low molecular weight poly(butylene adipate) soft segments and 4,4 diphenylmethane diisocyanate 1,4 butanediol hard segments.
i HTPB : hydroxyl terminated poly butadiene
j NC : nitrocellulose
k CEF : chloroethyl phosphate
l K10 : plasticizer (composition not known)
m BDNPA/F : bis-dinitropivalacetal/formal

Table 2.2. Weight and volume fractions of the components of PBX 9501.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Fraction</th>
<th>Volume Fraction^a</th>
</tr>
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<tbody>
<tr>
<td>HMX</td>
<td>0.949</td>
<td>0.92^b</td>
</tr>
<tr>
<td>Estane 5703</td>
<td>0.025</td>
<td>0.039</td>
</tr>
<tr>
<td>BDNPA/F</td>
<td>0.025</td>
<td>0.033</td>
</tr>
<tr>
<td>Irgonox</td>
<td>0.001</td>
<td>0.0</td>
</tr>
<tr>
<td>Voids</td>
<td>0.0</td>
<td>0.01-0.02</td>
</tr>
</tbody>
</table>

a The volume fraction data have been obtained from Dick et al. [5].
b McAfee et al. [6] cite volume fractions of 0.912 and 0.088 for HMX and binder respectively.
al. [4] are shown in Figure 2.1. The high strain rate Young’s modulus is around 12 times the low strain rate Young’s modulus at room temperature. The Poisson’s ratio of PBX 9501 is around 0.35 at room temperature. No data on the coefficient of thermal expansion of PBX 9501 have been found in the literature.

2.1.2 Particles - HMX

HMX crystals can exist in three stable phases (α-HMX, β-HMX, and δ-HMX) depending on temperature and pressure. Data obtained by Leiber [10] on these phases and their ranges of stability are shown in Table 2.3. The β-HMX phase is dominant at or near room temperature when linear elastic behavior is expected.

2.1.2.1 β-HMX crystal structure

The β-HMX crystal has a monoclinic structure as shown in Figure 2.2. The axis $b$ is the axis of second-order symmetry (or equivalently the plane $a\cdot c$ is the plane of symmetry). At room temperature the lattice parameters $a$, $b$ and $c$ are approximately in the ratio 6.5 : 11 : 7.5 and the angle $\beta$ is approximately 98° (Bedrov et al. [11]).

![Figure 2.1](image)

**Figure 2.1.** Young’s modulus of PBX 9501 (a) as a function of strain rate (b) as a function of temperature.
Table 2.3. Different phases of HMX and transition temperatures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Stable Region ($^\circ$ C)</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-HMX</td>
<td>103-162</td>
<td>$(\alpha \rightarrow \beta)$ at 116$^\circ$ C</td>
</tr>
<tr>
<td>$\beta$-HMX</td>
<td>20-103</td>
<td>$(\beta \rightarrow \delta)$ at 167-182$^\circ$ C</td>
</tr>
<tr>
<td>$\delta$-HMX</td>
<td>162-melt</td>
<td>$(\alpha \rightarrow \delta)$ at 193-201$^\circ$ C</td>
</tr>
</tbody>
</table>

Figure 2.2. Monoclinic structure of a $\beta$-HMX crystal.
2.1.2.2 Elastic moduli of $\beta$-HMX

Crystals of $\beta$-HMX behave in a mildly nonlinear elastic manner at ambient temperatures. With increase in temperature, voids develop in the crystals that lead to considerable degradation of elastic stiffness before melting. However, a linear elastic approximation is adequate for $\beta$-HMX below 40°C. The elastic constitutive relation for a monoclinic HMX crystal is shown in equation (2.1) [12] where the $b$ axis in Figure 2.2 (also referred to as the ‘2’ axis [13]) is the axis of second order symmetry.

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{31} \\
\sigma_{12}
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\
C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\
C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\
0 & 0 & 0 & C_{44} & 0 & C_{46} \\
C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\
0 & 0 & 0 & C_{46} & 0 & C_{66}
\end{bmatrix}
\begin{bmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
\epsilon_{33} \\
\epsilon_{23} \\
\epsilon_{31} \\
\epsilon_{12}
\end{bmatrix}
\] (2.1)

Linear elastic moduli of $\beta$-HMX have been determined experimentally by Zaug [14] and Dick et al. [5] from measurements of wave velocities through single crystals. Molecular dynamics (MD) simulations by Sewell et al. [15] have also been used to estimate the stiffness matrix of $\beta$-HMX. The stiffness matrix of $\beta$-HMX from experiments and MD simulations is shown in Table 2.4. The values of the 13 elastic coefficients shown in the table were calculated by Zaug at a temperature of 107°C using a nonlinear least squares simplex fit of the experimental data using the room temperature value of bulk modulus (12.5 GPa) as a benchmark. The molecular dynamics simulations by Sewell et al. (shown inside round brackets in Table 2.4) are observed to be quite close to the experimental values.

2.1.2.3 Thermal expansion of $\beta$-HMX

The coefficients of thermal expansion (CTEs) of HMX crystals shown in Table 2.5 have been determined both from X-ray diffraction experiments [16] and from MD simulations [11]. The values show a pronounced anisotropy in the $b$ lattice direction compared to the $a$ and $c$ directions. Although the angles $\alpha$ (between the $a$ and $b$ lattice directions) and $\gamma$ (between the $a$ and $c$ lattice directions) do not vary significantly with temperature, there is a large change in the angle $\beta$ of the monoclinic lattice.
Table 2.4. The stiffness matrix of $\beta$-HMX [14, 15]. All values are in GPa. Numbers inside round brackets are from MD simulations [15].

<table>
<thead>
<tr>
<th></th>
<th>19.8 (18.7)</th>
<th>3.9 (4.9)</th>
<th>12.5 (7.7)</th>
<th>0</th>
<th>0.5 (-1.7)</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>26.3 (17.0)</td>
<td>6.5 (7.3)</td>
<td>0</td>
<td>-1.4 (3.0)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.9 (16.7)</td>
<td>0</td>
<td>0.1 (0.2)</td>
<td>0</td>
<td></td>
<td>2.8 (8.9)</td>
</tr>
<tr>
<td>Symm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.4 (9.3)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.6 (9.8)</td>
</tr>
</tbody>
</table>

Table 2.5. Thermal expansion properties of $\beta$-HMX.

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Expts. ($\times10^{-5}$/K) (Herrmann [16])</th>
<th>MD ($\times10^{-5}$/K) (Bedrov et al. [11])</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.29</td>
<td>2.07</td>
</tr>
<tr>
<td>Linear/Angular</td>
<td>b</td>
<td>11.60</td>
</tr>
<tr>
<td>Expansion</td>
<td>c</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>Volume Expansion</td>
<td>13.1</td>
</tr>
</tbody>
</table>
2.1.2.4 Particle size distribution in PBX 9501

The dry blend of HMX particles in PBX 9501 is a mixture of two different size distributions of particles. The coarse HMX particles are sized between 44 and 300 microns while the fine particles are less than 44 microns in size. The particles are mixed in a 3 to 1 ratio of coarse to fine particles. In the composite, the smaller particles fit into the interstitial spaces between the larger ones. The large particles occupy most of the volume of the composite. A particle distribution for the dry blend is shown in Table 2.6.

The manufacture of PBX 9501 involves mixing the dry blend of HMX and the binder to form molding powder granules (prills) of PBX 9501. These powders are then isostatically compressed at 90°C until the porosity is reduced to 1-2% and the pressed form of PBX 9501 is obtained. The size distribution of HMX particles in PBX 9501 after processing is significantly different from that before processing. Experiments by Skidmore et al. [17] have shown that the cumulative volume fraction of the finer sized particles is dramatically higher in pressed PBX 9501 compared to the dry blend. Figure 2.3 shows the particle size distributions of HMX in the dry blend and in pressed PBX 9501. Experiments by Skidmore et al. [18] have shown that the consolidation of prills initially involves little damage to the large HMX crystals. As porosity is decreased, there is an increasing incidence of transgranular cracking and twinning in the large HMX crystals. If porosity is decreased to less that 1%, microcracks grow across crystals due to crystal-to-crystal contact and intercrystalline indentation.

2.1.3 Binder - Estane 5703 and BDNPA/F

The binder in PBX 9501 is essentially a combination of Estane 5703 and a plasticizer (BDNPA-F). A free radical inhibitor (Irgonox) is added for further stability of PBX 9501. Estane 5703 is amorphous and thermoplastic with a relatively low glass transition temperature (-31°C) and a melting temperature of around 105°C. It contains soft and hard segments that serve to enhance entanglement and leads to low temperature flexibility, high temperature stability and good adhesive properties. The plasticizer (BDNPA/F) decreases the binder strength and stiffness.
Table 2.6. HMX particle size distributions in the PBX 9501 dry blend [8].

<table>
<thead>
<tr>
<th>Particle Size (microns)</th>
<th>Coarse HMX (Wt. %)</th>
<th>Fine HMX (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 44</td>
<td>3-13%</td>
<td>at least 75%</td>
</tr>
<tr>
<td>≤ 74</td>
<td>14-26%</td>
<td></td>
</tr>
<tr>
<td>≤ 125</td>
<td>40-60%</td>
<td>100%</td>
</tr>
<tr>
<td>≤ 149</td>
<td>84-96%</td>
<td></td>
</tr>
<tr>
<td>≤ 297</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.3. HMX particle size distributions in PBX 9501 at various stages of processing (adapted from [17]).
2.1.3.1 Elastic moduli of PBX 9501 binder

The elastic properties of the PBX 9501 binder are sensitive to strain rate and temperature. Binder moduli are difficult to determine experimentally because of the low stiffness of the material. Moduli from MD simulations of the binder constituents are not yet available. Approximate elastic moduli of the PBX 9501 binder from experiments performed by Dick et al. [5], Cady et al. [7, 19], Gray et al. [4] and Wetzel [8] at various strain rates and temperatures are shown in Figure 2.4. The Young’s modulus of the binder shows considerable scatter at high strain rates. The Poisson’s ratio of the binder is close to 0.5, as can be expected of rubbers and elastomers.

2.1.3.2 Thermal expansion of PBX 9501 binder

Wetzel [8] cites the coefficient of thermal expansion of Estane 5703 to be between $10^{-5}$ to $20\times10^{-5}$/K. Since data are not available for the binder, the coefficient of thermal expansion of the PBX 9501 binder is assumed to be the same as that of Estane 5703.

![Figure 2.4](image_url)

**Figure 2.4.** Young’s modulus of PBX 9501 binder (a) as a function of strain rate (b) as a function of temperature.
2.1.4 Mock polymer-bonded explosives

Mock polymer bonded explosives containing glass beads or sugar instead of explosive particles have also been studied by various researchers [7, 8]. These mock materials can be easily tested in the laboratory and can be used to validate micromechanics methods for the prediction of effective properties of polymer bonded explosives.

2.2 Micromechanics of composites

The term “micromechanics” describes a class of methods for determining the effective material properties of composites given the material properties of the constituents. In these methods, governing equations based on continuum approximations are used to determine effective properties. The material properties of interest in this work are the linear elastic moduli and coefficients of thermal expansion of PBXs. The high volume fraction of the dispersed component in PBXs as well as the high modulus contrast between the dispersed and the continuous components provide the main challenges. In this section, some rigorous bounds and analytical approximations for effective moduli are reviewed and the effectiveness of these methods is discussed in the context of PBX 9501 at room temperature and under low strain rates. In addition, numerical methods of calculating effective properties are also reviewed.

2.2.1 Rigorous bounds

The most elementary rigorous bounds on elastic moduli are the Voigt (arithmetic mean) and Reuss (harmonic mean) bounds [20] which can be written as

\[
K_{\text{eff}}^U = \langle K \rangle, \quad G_{\text{eff}}^U = \langle G \rangle, \quad \text{Voigt Bounds} \quad (2.2)
\]

\[
1/K_{\text{eff}}^L = \langle 1/K \rangle, \quad 1/G_{\text{eff}}^L = \langle 1/G \rangle, \quad \text{Reuss Bounds} \quad (2.3)
\]

where, for a quantity \( a \), \( \langle a \rangle = a_p f_p + a_b f_b \); \( f_p, f_b \) are particle and binder volume fractions; \( K_p, K_b, K_{\text{eff}} \) are particle, binder and composite bulk moduli; and \( G_p, G_b, G_{\text{eff}} \) are particle, binder and composite shear moduli. The superscripts \( U \) and \( L \) denote upper and lower bounds on an effective property.
2.2.1.1 **Hashin-Shtrikman bounds**

Variational principles based on the concept of a polarization field have been used by Hashin and Shtrikman [21] to obtain improved bounds on the effective elastic moduli that have been shown to be optimal for assemblages of coated spheres. For particulate composites these bounds can be written as

\[
K_{\text{eff}}^U = \langle K \rangle - \frac{3f_p f_b (K_p - K_b)^2}{3 \langle K \rangle + 4G_p}, \quad \text{Hashin-Shtrikman Upper Bounds} \quad (2.4)
\]

\[
G_{\text{eff}}^U = \langle G \rangle - \frac{6f_p f_b (G_p - G_b)^2}{6 \langle G \rangle + 5\Lambda}, \quad (2.5)
\]

\[
\frac{1}{K_{\text{eff}}^L} = \frac{1}{\langle K \rangle} - \frac{4f_p f_b (1/K_p - 1/K_b)^2}{4 \langle 1/K \rangle + 3/G_b}, \quad \text{Hashin-Shtrikman Lower Bounds} \quad (2.6)
\]

\[
\frac{1}{G_{\text{eff}}^L} = \frac{1}{\langle G \rangle} - \frac{f_p f_b (1/G_p - 1/G_b)^2}{\langle 1/G \rangle + \Upsilon}, \quad (2.7)
\]

where, for a quantity \( a \), \( \langle a \rangle = a_p f_b + a_b f_p \); and

\[
\Lambda = G_p \left( \frac{9K_p + 8G_p}{K_p + 2G_p} \right), \quad \Upsilon = \frac{1}{G_b} \left( \frac{3K_b + 4G_b}{9K_b + 8G_b} \right). \quad (2.8)
\]

Bounds on the effective coefficient of thermal expansion of a two-component isotropic composite can be calculated using the Hashin-Shtrikman bounds [22]. These bounds are

\[
\alpha_{\text{eff}}^U = \langle \alpha \rangle + \frac{4f_p f_b G_b (K_b - K_p)(\alpha_b - \alpha_p)}{3K_p K_b + 4G_b \langle K \rangle}, \quad \text{Rosen-Hashin Upper Bound} \quad (2.9)
\]

\[
\alpha_{\text{eff}}^L = \langle \alpha \rangle + \frac{4f_p f_b G_p (K_b - K_p)(\alpha_b - \alpha_p)}{3K_p K_b + 4G_p \langle K \rangle}, \quad \text{Rosen-Hashin Lower Bound} \quad (2.10)
\]

where \( \alpha_p, \alpha_b, \alpha_{\text{eff}} \) are the coefficients of thermal expansion of particles, binder and composite, respectively.

2.2.1.2 **Third-order bounds**

Third-order bounds [23] improve upon the Hashin-Shtrikman bounds by using three-point correlation functions [24, 25] to incorporate geometric information into the de-
termination of upper and lower bounds on effective properties. These bounds can be expressed as

\[ K_{\text{eff}}^{U} = \langle K \rangle - \frac{3 f_p f_b (K_p - K_b)^2}{3\langle K \rangle + 4 \langle G \rangle_\zeta}, \]  
Third-order Upper Bounds \hspace{1cm} (2.11)

\[ G_{\text{eff}}^{U} = \langle G \rangle - \frac{6 f_p f_b (G_p - G_b)^2}{6\langle G \rangle + \Theta}, \]  
(2.12)

\[ \frac{1}{K_{\text{eff}}} = \langle 1/K \rangle - \frac{4 f_p f_b (1/K_p - 1/K_b)^2}{4\langle 1/K \rangle + 3 \langle 1/G \rangle_\zeta}, \]  
Third-order Lower Bounds \hspace{1cm} (2.13)

\[ \frac{1}{G_{\text{eff}}} = \langle 1/G \rangle - \frac{f_p f_b (1/G_p - 1/G_b)^2}{\langle 1/G \rangle + 6\Xi}, \]  
(2.14)

where, for a quantity \( a \), \( \langle a \rangle_\zeta = a_p \zeta_p + a_b \zeta_b \), and \( \langle a \rangle_\eta = a_p \eta_p + a_b \eta_b \). Also,

\[ \Xi = \frac{10 \langle K \rangle^2 \langle 1/K \rangle_\zeta + 5 \langle G \rangle \langle 3G + 2K \rangle \langle 1/G \rangle_\zeta + \langle 3K + G \rangle^2 \langle 1/G \rangle_\eta}{9K + 8G} \]  
(2.15)

\[ \Theta = \frac{10 \langle G \rangle^2 \langle K \rangle_\zeta + 5 \langle G \rangle \langle 3G + 2K \rangle \langle G \rangle_\zeta + \langle 3K + G \rangle^2 \langle G \rangle_\eta}{K + 2G^2} \]  
(2.16)

These bounds depend on two extra geometric parameters, \( \zeta_p = 1 - \zeta_b \) and \( \eta_p = 1 - \eta_b \) which incorporate the three-point correlation functions and have been found to lie between 0 and 1. If the assumption is made that the penetrable spheres model (where spheres placed randomly in the RVE may overlap) is representative of high volume fraction particulate composites, the values of \( \zeta_p \) and \( \eta_p \) listed by Berryman [26] can be extrapolated to a volume fraction of 0.92 to obtain \( \zeta_p = 0.956 \) and \( \eta_p = 0.937 \). These values have been used to calculate third-order bounds for PBX 9501.

### 2.2.1.3 Comparison of bounds

Table 2.7 shows the data used to compute the Voigt-Reuss, Hashin-Shtrikman and third-order bounds for PBX 9501 shown in Table 2.8. The elastic moduli of HMX in Table 2.7 are based on bounds provided by Zaug [14]. The elastic moduli of the binder and PBX 9501 are based on an average of the low strain rate data. The coefficients of thermal expansion are from Bedrov et al. [11].

The third-order bounds in Table 2.8 provide the best estimates of the elastic moduli of PBX 9501 of the three. Lower bounds are closer to the experimental data than upper
Table 2.7. Elastic moduli and CTE of PBX 9501 and its components at room temperature and low strain rate.

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume Fraction (%)</th>
<th>Young’s Modulus (MPa)</th>
<th>Poisson’s Ratio</th>
<th>Bulk Modulus (MPa)</th>
<th>Shear Modulus (MPa)</th>
<th>CTE (10⁻⁵/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX</td>
<td>92</td>
<td>15300</td>
<td>0.32</td>
<td>14300</td>
<td>5800</td>
<td>11.6</td>
</tr>
<tr>
<td>Binder</td>
<td>8</td>
<td>0.7</td>
<td>0.49</td>
<td>11.7</td>
<td>0.23</td>
<td>20</td>
</tr>
<tr>
<td>PBX 9501</td>
<td>1000</td>
<td>0.35</td>
<td>1111</td>
<td>370</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.8. Bounds on properties of PBX 9501.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Modulus (MPa)</th>
<th>Shear Modulus (MPa)</th>
<th>Thermal Expansion (×10⁻⁵/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Bounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voight</td>
<td>13034</td>
<td>5332</td>
<td>-</td>
</tr>
<tr>
<td>Hashin-Shtrikman</td>
<td>11372</td>
<td>5257</td>
<td>12.3</td>
</tr>
<tr>
<td>Third-order</td>
<td>11306</td>
<td>4959</td>
<td>-</td>
</tr>
<tr>
<td>PBX 9501 (Experiments)</td>
<td>1111</td>
<td>370</td>
<td>-</td>
</tr>
<tr>
<td>Lower Bounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Third-order</td>
<td>224</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>Hashin-Shtrikman</td>
<td>148</td>
<td>11</td>
<td>11.6</td>
</tr>
<tr>
<td>Reuss</td>
<td>144</td>
<td>3</td>
<td>-</td>
</tr>
</tbody>
</table>

bounds. The best lower bound predicts effective bulk and shear moduli that are about 20% of the bulk and shear moduli of PBX 9501. This implies that accurate estimates of the effective elastic moduli of PBXs cannot be obtained from rigorous bounds at low strain rates and ambient temperature. On the other hand, the bounds on the coefficient of thermal expansion of PBX 9501 are within 6% of each other. Therefore, these bounds can be used to estimate the CTEs of some PBXs.

2.2.2 Analytical methods

Analytical methods for approximating effective elastic moduli of random composites have been developed by researchers since the early 1900s. Early developments were based on dilute dispersions of particles in a continuous matrix assuming that there were no particle-particle interactions. More recent developments have explored concentrated
dispersions where particle-particle interactions are allowed. For high volume fraction particulate composites, the composite spheres assemblage, self-consistent schemes, and the differential effective medium approach are of interest.

The effective CTE of an isotropic composite containing isotropic components can be determined exactly, provided the effective bulk modulus of the composite is known, using the expression \[ \alpha_{\text{eff}} = \langle \alpha \rangle - K_p K_b \left( \frac{\alpha_p - \alpha_b}{K_p - K_b} \right) \left( \frac{1}{K_{\text{eff}}} - \langle 1/K \rangle \right). \] (2.17)

### 2.2.2.1 Composite spheres assemblage (CSA)

The composite spheres assemblage model [27] idealizes a particulate composite with spherical particles coated by a layer of binder. The volume of the composite is assumed to be filled completely with various sizes of these coated spheres. The ratio of the radius of a spherical particle to the thickness of its coating reflects the volume fraction of particles in the composite. The solution of the problem involves placing a coated sphere in the effective medium and applying a hydrostatic stress at the boundary of the coated sphere. This approach leads to an expression for the effective bulk modulus that can be written as

\[ K_{\text{eff}} = K_b + f_p \left( \frac{1}{K_p - K_b} + \frac{f_b}{K_b + 4/3G_b} \right)^{-1}. \] (2.18)

Expressions for the effective shear modulus from the CSA model are available that are valid in the limit of low particle volume fraction (the dilute approximation). However, for high concentrations of particles, the shear modulus cannot be found accurately using the CSA model.

### 2.2.2.2 Self-consistent schemes (SCS)

The effective stiffness tensor of a dilute distribution of particles in a continuous binder can be expressed as [28]

\[ C_{\text{eff}} = C_b + f_p (C_p - C_b) : A(C_p, C_b) + O(f_p) \] (2.19)

where \( C_p, C_b, C_{\text{eff}} \) are the stiffness tensors of the particles, binder, and composite, and \( A \) is the tensor that relates the applied strain to the strain in a particle. When the volume
fractions of particles is more than 5%, the binder in the dilute approximation is replaced with a material that possesses the unknown effective elastic properties of the composite. Thus, the expression for the effective stiffness tensor is changed to

$$\mathbf{C}_{\text{eff}} = \mathbf{C}_b + f_p(\mathbf{C}_p - \mathbf{C}_b) : \mathbf{A}(\mathbf{C}_p, \mathbf{C}_{\text{eff}}) + O(f_p).$$  \tag{2.20}$$

The above equation can be solved for the effective stiffness of the composite for various particle shapes. This procedure is called the “self-consistent scheme”, the “effective medium approximation” and also the “coherent potential approximation”. Various types of “self-consistent” approximations of effective composite properties can be found in the literature [29, 30]. For a particulate composite containing a dispersion of elastic spheres, the commonly used self-consistent scheme leads to the following equations in $K_{\text{eff}}$ and $G_{\text{eff}}$ that are solved iteratively.

$$K_{\text{eff}} = K_b + f_p \left[ \frac{1}{K_p - K_b} + \left( \frac{3}{3K_{\text{eff}} + 4G_{\text{eff}}} \right) \frac{K_p - K_{\text{eff}}}{K_p - K_b} \right]^{-1}, \tag{2.21}$$

$$G_{\text{eff}} = G_b + f_p \left[ \frac{1}{G_p - G_b} + \left( \frac{12 + 6K_{\text{eff}}/G_{\text{eff}}}{15K_{\text{eff}} + 10G_{\text{eff}}} \right) \frac{G_p - G_{\text{eff}}}{G_p - G_b} \right]^{-1}. \tag{2.22}$$

2.2.2.3 Differential effective medium approach (DEM)

The differential effective medium approach has been successfully applied to approximate the effective properties of composites containing particles in a continuous binder, mostly for low volume fractions of particles [28, 29, 31]. In this approach, an infinitesimal volume of particles is added to the binder and the effective properties are calculated using a dilute approximation. The binder is then replaced by the effective material, an infinitesimal volume of particles added, and the effective properties calculated. This process is repeated until the actual volume fraction of particles is obtained. This approach can be represented by the following coupled system of linear first order ordinary differential equations that can be solved using a fourth-order Runge-Kutta scheme.

$$1 - f_p \frac{dK_{\text{eff}}}{df_p} = (K_p - K_{\text{eff}}) \left( \frac{K_{\text{eff}} + 4/3G_{\text{eff}}}{K_p + 4/3G_{\text{eff}}} \right),$$  \tag{2.23}$$

$$1 - f_p \frac{dG_{\text{eff}}}{df_p} = (G_p - G_{\text{eff}}) \left( \frac{G_{\text{eff}} + \varphi}{K_p + \varphi} \right), \tag{2.24}$$
where

$$\varphi = \frac{G_{\text{eff}}}{6} \left( \frac{9K_{\text{eff}} + 8G_{\text{eff}}}{K_{\text{eff}} + 2G_{\text{eff}}} \right).$$

Several other approximation schemes exist that generate analytical equations relating the effective elastic moduli to the constituent moduli and volume fractions. Details of these approaches can be found in the monograph by Milton [32].

### 2.2.2.4 Comparison of analytical approaches

Estimates of the effective properties of PBX 9501 using analytical approaches are shown in Table 2.9. The properties of the components of PBX 9501 listed in Table 2.7 have been used in these calculations. The bulk modulus estimate from the composite spheres assemblage approach matches the lower bound predicted by the Hashin-Shtrikman bounds and is considerably lower than the experimentally determined bulk modulus. The values of the bulk and shear modulus predicted by the self-consistent scheme are about 10 times the experimental values. The differential effective medium estimates are improvements over the third-order bounds discussed before. These estimates are still considerably lower than the experimentally determined moduli. The estimates of CTE depend on the accuracy of the estimates of bulk modulus. However, for PBX 9501, the low CTE contrast of the two components leads to approximately the same value of effective CTE. In fact, considering the large modulus contrast between the particle and the binder, the differential effective medium estimates are quite accurate and can be used when no better approximations are available.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Modulus (MPa)</th>
<th>Shear Modulus (MPa)</th>
<th>Thermal Expansion ($\times 10^{-5}$/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite Spheres</td>
<td>148</td>
<td>-</td>
<td>12.3</td>
</tr>
<tr>
<td>Self-consistent Scheme</td>
<td>11044</td>
<td>4700</td>
<td>12.9</td>
</tr>
<tr>
<td>Diff. Effective Medium</td>
<td>229</td>
<td>83</td>
<td>12.5</td>
</tr>
<tr>
<td>Experiments</td>
<td>1111</td>
<td>370</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2.3 Numerical approximations

The effective elastic moduli of a particulate composite can be determined approximately by determining the stresses and strains in a representative volume element under appropriate boundary conditions using numerical methods. The effective stiffness tensor $C_{ijkl}^{\text{eff}}$ of the composite can then be obtained from the relation

$$\langle \sigma_{ij} \rangle_V = C_{ijkl}^{\text{eff}} \langle \epsilon_{kl} \rangle_V$$

(2.25)

where $\langle \sigma_{ij} \rangle_V$ are the volume averaged stresses and $\langle \epsilon_{ij} \rangle_V$ are the volume averaged strains.

The earliest numerical approximations of effective elastic moduli were carried out using finite difference schemes [33, 34]. These were two-dimensional approximations for regular arrays of fibers in a matrix. Randomly generated microstructures in two dimensions were simulated soon after these preliminary investigations [35]. More recently, researchers have approached this problem using finite element methods [36, 37], boundary integral methods [38, 39, 40], Fourier transform based methods [41, 42], and the method of cells [43]. Three-dimensional simulations are also increasingly being carried out [44, 45].

2.2.3.1 The representative volume element

The representative volume element (RVE) is conceptually similar to the crystallographic unit cell which is the building block in the structure of crystals [46]. Indeed, unit cells are the most commonly used RVEs. The size of the RVE and the amount of geometrical detail modeled has been determined primarily by the availability of computational power. Though Sab [47] has shown that the effective properties of a random composite can be calculated by the simulation of one single RVE, this single RVE is not easy to determine. A more practical approach is to simulate a large number of smaller RVEs so that some statistics on the effective properties are obtained. For a composite containing randomly distributed monodisperse spheres, the RVE size is about two sphere diameters [48] if only effective elastic properties are required. However, such rules of thumb are not available for other types of random particulate composites.

In two-dimensional studies, the microstructure of particulate composites has been modeled with monodisperse circular particles [49], square particles [50], and arbitrarily
shaped particles [51]. The particles have been placed in a random sequential manner in the RVE in all these studies. Two-dimensional models of PBXs have also used circular and square particles distributed using a molecular dynamics based approach [52]. Some attempts have also been made to create RVEs from digitized micrographs of PBXs [53].

Most studies of particulate composites deal with two-dimensional microstructures. However, a few three-dimensional studies have also been performed [54, 44, 55]. A commonly used procedure for three-dimensional microstructure generation is random sequential placement of spherical/cubical particles in a RVE. This approach is not suitable for high volume fraction composites like PBX 9501 because sequential placement of particles becomes extremely inefficient beyond volume fractions of 45%. The molecular dynamics based approach of Baer [52] is an improvement over sequential placement. However, locking of particles leads to maximum achievable volume fractions of around 70%. A more practicable approach, for PBX-like materials, is the digital image processing based method adopted by Garbozci and Day [54]. In this method, X-ray tomography is used to generate three-dimensional voxelized images of the composite. Terada et al. [55] have also developed detailed digital image based models of composites that use two-dimensional slices to generate three-dimensional microstructures. Though digital techniques appear lucrative, advanced image processing techniques are required to generate microstructures for PBX 9501 because the high volume fractions and similar densities and reflectivities of particles and binder make it difficult to identify the components of the composite from images.

2.2.3.2 Finite element approximations

Random particulate composites containing low volume fractions of particles can be approximated by square arrays of fibers in two dimensions [49] and cubic arrays of spheres in three dimensions [36]. Displacement based finite element solutions have been found to predict effective properties that overestimate the actual properties while force-based solutions provide a lower bound on the actual properties. A recent study, performed on regular arrays of fibers by Pecullan et al. [56], has found that the force based effective stiffness tensor is more accurate for a composite with high modulus contrast and
a compliant matrix. Force based finite element methods are not utilized in this research because of the difficulties in formulation and implementation of these methods. The multiphase finite element method [57] is a variation of the standard displacement-based finite element approach. In this method, different material properties are assigned to different Gauss points in the finite element analysis of a complex microstructure. This approximation eliminates the need to generate complex meshes to describe the geometry. However, the robustness of the method is still not very well established.

Ramakrishnan et al. [51] have used a generalized plane strain approach to model particulate metal matrix composites where particles of various shapes and sizes were randomly distributed in a two-dimensional square RVE. The effective Young’s modulus was determined by the application of a uniform unidirectional displacement. The effective bulk modulus was determined by applying equal displacements in the three orthogonal directions. It is observed that the shapes of the particles do not have any significant effect on the effective elastic properties even though many particles have sharp acute angles and therefore high stress concentrations.

Random distributions of particles in two dimensions have also been studied by Theo-caris et al. [58] in the context of determining the effective Poisson’s ratio. Finite element simulations were performed on a unit cell with periodic boundary conditions and uniform pre-stresses. The effective elastic properties were determined using a strain energy match between a cell simulating the microstructure and an equivalent homogeneous cell. This study shows that Poisson’s ratios calculated using two-dimensional models are actually two-dimensional Poisson’s ratios that have an upper bound of 1.0 instead of the 0.5 for the three-dimensional case. The study also suggests that sharp corners in particles do not have any significant effect on the effective elastic properties - assuming perfect interfacial bonding.

A two-step approach has been used by Jia and Povirk [50] to model a two-phase composite containing randomly distributed square inclusions. In this approach, a window of the RVE is chosen in the first stage of the calculations and moved over the RVE. Two-dimensional displacement based finite elements are used to calculate the effective properties at each location of the window. These effective properties are then assigned
to a smaller mesh for faster calculations of the overall properties. The study finds that the error in the estimation is small for the component properties considered. Pecullan et al. [56] have also observed that replacement of the smallest scale microstructure by the equivalent homogeneous material does not cause large errors in calculation of the effective stiffness tensors. This result is of interest in this research because generation of microstructures occupying more that 86% of the volume is difficult. Instead, we can generate microstructures that occupy about 86% of the volume and replace the remaining volume with a “dirty” binder (a binder with the effective properties of a mixture of particles and the original binder) without much loss in accuracy.

In the three-dimensional study by Gusev [44], RVEs containing spheres have been modeled using displacement-based finite elements. The microstructure was discretized using tetrahedral finite elements. This approach is not suitable for high volume fraction composites like PBX 9501 because the meshing of close-packed particles using tetrahedral elements leads to extremely skewed elements and poor numerical accuracy. Finite element meshes are easier to generate from three-dimensional voxelized images [54, 55] where each voxel is then modeled as an eight-noded linear displacement finite element.

A question that arises for PBXs is whether the binder “wets” all the particles. In other words, it is of interest to know the amount of strain that leads to interfacial debonding between the particles and the binder. A three-dimensional finite element study of the effect of interfaces on the stresses in composites containing spherical inclusions arranged in a cubic array has been carried out by Dong and Wu [59]. The results indicate that the assumption of perfect bonding used in many micromechanics studies may not be appropriate for high concentrations of particles even when small strains are applied because very high interfacial stresses are developed.

2.2.3.3 Homogenization theory

The mathematical theory of homogenization [60] is an established approach for determining effective properties of periodic composites [61]. In this method, the governing differential equations with rapidly varying coefficients are replaced by differential equations with constant or slowly varying coefficients. Asymptotic expansions of the field variables along with the assumption of periodicity lead to this transformed set of
equations. The modified problem, called the Y-periodic homogenization problem, is then solved using finite elements or other techniques.

Ghosh and co-workers [62, 37] have used homogenization theory along with the Voronoi cell finite element method to model RVEs containing random distributions of particles at volume fractions of up to 50%. In this approach, particle locations are generated within the RVE using a random process. A weighted Voronoi tessellation of these particles is carried out to generate a set of Voronoi cells each containing a single particle. Homogenization theory is used to model the effect of a single particle on the properties of a Voronoi cell. The approach shows good agreement with detailed finite element analyses of the same microstructure. However, for high particle volume fractions (> 80%) a weighted Voronoi tessellation can lead to needle shaped cells in two dimensions. In three dimensions, generation of weighted Voronoi tessellations is considerably involved. These considerations make this approach unsuitable for high volume fraction particulate composites.

2.2.3.4 Stochastic finite elements

In continuum descriptions of composites, the constitutive relationship is only a function of spatial position. Stochastic descriptions of the constitutive relation assume that the stiffness tensor is a random field with continuous realizations. In other words, an additional “stochastic” variable is added to the continuum description. Stochastic finite element analyses attempt to solve this modified problem using finite element techniques. These methods are applicable to particulate composites where the particle distributions can vary in a random manner.

Ostoja-Starzewski [63] has performed stochastic finite element analyses on two-dimensional composites reinforced by randomly located disks. Numerous simulations have been carried out to obtain bounds on the effective stiffness tensor. These analyses show, for a given RVE size, that the predicted bounds deviate from each other by 0.5% as the modulus contrast between the components reaches about 20. Huyse and Maes [64] have used stochastic finite element analyses (using a truss network to represent a particulate composite) to determine the autocorrelation and cross-correlation coefficients between various elastic constants. Ostoja-Starzewski [65] has suggested that
these correlation coefficients could be easily determined for particulate composites. This information could be then be used to generate bounds on the effective elastic response without resorting to time consuming numerical simulations of different realizations of the microstructure.

2.2.3.5 Discrete models

Discrete models, e.g., spring network models, are receiving renewed attention because they are easier to generate and faster to solve. Two-dimensional triangular spring network models have been used by Day et al. [66] to determine the effective elastic response of plates containing randomly located holes. Toi and Kiyoshe [67] used a three dimensional discrete model consisting of springs and rigid crystals to determine the effective mechanical properties of polycrystals with damage. Network based approximations for high contrast, high volume fraction composites have also been developed by Berlyand and Kolpakov [68]. These models generate quite accurate results. Voronoi tessellations of the geometry are required in some of these models and the associated problems of generating these tessellations for high volume fraction materials make these models unattractive for PBXs. On the other hand, digital images of random composites can easily be resolved into spring networks though some involved image processing is necessary to obtain suitable images of PBXs.

2.2.3.6 Integral equation methods

Boundary integral based methods have been used with some success for determining the effective mechanical and thermal properties of two-dimensional composites (e.g., Rizzo and Shippy [38], Achenbach and Zhu [39], Papathanasiou et al. [69], Helsing [70, 71]). The computations of Rizzo and Shippy [38] for square inclusions avoided calculations of stresses at the corner singularity regions. The calculations of Achenbach and Zhu [39] were carried out on single circular inclusions using standard boundary element techniques. Similar methods have been used to determine the effective elastic moduli of two-dimensional composites with low volume fractions of circular inclusions by Papathanasiou et al. [69].

The interface integral method of Helsing [71, 72] has been used to generate accurate
effective elastic properties of periodic composites in two dimensions. An Airy stress function based complex variable representation of the governing differential equation is converted into the Sherman-Lauricella type integral equation in this technique. The integral equation is solved using a matrix free Nyström algorithm [71]. The Helsing method has been used to determine accurate effective elastic moduli of RVEs containing large numbers of complex shaped inclusions nearly in contact [73]. This technique promises to be one of the best available for two-dimensional analysis of the low strain rate micromechanics of composites. It is especially suited for problems that involve stress singularities. The use of complex variables leads to the method being applicable only to two-dimensional problems in its current form. If the particles touch each other or have high modulus contrast, convergence is reported to be relatively slow. The implementation of the Nyström algorithm consists of several steps and is quite involved, making this method unattractive for this research.

2.2.3.7 Fourier transform method

Complex microstructures have also been studied by Moulinec and Suquet [41] using a Fourier transform based numerical approach to solve the unit cell problem. This approach takes advantage of the assumed periodicity of the elastic fields and by reducing the governing differential equations to the Lippman-Schwinger equation form both in real space and Fourier space. The solution is then obtained using an explicit algorithm that alternates between the real and the Fourier spaces. Discretization of the problem is carried out using a regular grid of pixels or voxels generated from images of microstructures. The advantage of this method is that special consideration is not required for materials that are nearly incompressible (as is needed to avoid element locking in finite element approaches). However, for high modulus contrast between the components, the rate of convergence is slow. This problem has been partially solved using an accelerated convergence method [42, 74] that converges as the square root of the modulus contrast. The Fourier transform based method is attractive because it can easily be extended to model three-dimensional problems and inelastic material behavior in PBXs.
2.2.3.8 Generalized method of cells

The generalized method of cells (GMC) [43, 75] has been used to model the micromechanical behavior of different types of composites with relative success. The advantage of this method over other numerical techniques is that the full set of effective elastic properties can be calculated in one step instead of solving a number of boundary value problems with different boundary conditions. The problem of discretization is also minimized because a regular rectangular grid is used. GMC uses an averaging technique that satisfies subcell continuity and equilibrium in an average sense using integrals over subcell boundaries. This method has been shown to be more computationally efficient than finite elements for modeling fiber composites [76]. However, the computational efficiency of GMC decreases and can become worse than that of finite elements as the number of subcells increases because the size of the matrix that is inverted is the square/cube of the number of subcells in two/three dimensions. This leads to large memory requirements and large computational times while modeling complex microstructures. The computational efficiency of GMC has been improved after reformulation by Pindera and Bednarcyk [77, 78, 79, 80]. The reformulation has taken advantage of the continuity of tractions across subcells to obtain a system of equations in three dimensions.

There is a lack of coupling between the normal and shear stresses and strains in GMC. Bednarcyk and Arnold [81] claim that this lack of coupling makes for an “ultra-efficient” micromechanics model. However, this lack of coupling leads to the gross underestimation of shear moduli. Recently, Williams and Aboudi [82] have attempted to rectify the shear-coupling problem for periodic arrays of fibers using a third order expansion for the displacement field. However, this approach leads to a large system of equations and the efficiencies introduced by Pindera and Bednarcyk are no longer applicable. An alternative approach has been taken by Gan et al. [83] to include normal-shear coupling in the GMC analysis. The original GMC assumes that there is traction continuity across all cell and subcell interfaces. The modification made by Gan et al. removes this constraint and instead attempts to satisfy subcell equilibrium and compatibility. Results obtained by the new method show a much better prediction of shear moduli than the original GMC.
CHAPTER 3

MICROMECHANICS SIMULATIONS OF
GLASS-ESTANE MOCK POLYMER
BONDED EXPLOSIVES

3.1 Abstract

Polymer bonded explosives (PBXs) are particulate composites containing explosive particles and a continuous binder. The explosive particles occupy high volume fractions, often greater than 90%. Additionally, the elastic modulus of the particles, at room temperature and higher, is often three to four orders of magnitude higher than that of the binder. Both experimental and numerical determination of macroscopic properties of these composites is difficult. High modulus contrast mock polymer bonded explosives provide a means of relatively inexpensive experimentation and validation of numerical approaches to determine properties of these materials. The goal of this investigation is to determine whether the effective elastic properties of monodisperse glass-estane mock polymer bonded explosives can be predicted from two-dimensional micromechanics simulations using the finite element method. In this study, the effect of representative volume element size on the prediction of two-dimensional properties is explored. Two-dimensional estimates of elastic properties are compared with predictions from three-dimensional computations and with experimental data on glass-estane composites containing three different volume fractions of spherical glass beads. The effect of particle debonding on the effective elastic properties is also investigated using contact analyses. Results show that two-dimensional unit cells containing 10 to 20 circular particles are adequate for modeling glass-estane composites containing less than 60% glass particles by volume. No significant difference is observed between properties predicted by the two- and three-dimensional models. Finite element simulations of
representative volume elements, containing particles that are perfectly bonded to the
binder, produce estimates of Young’s modulus that are higher than the experimental
data. Incorporation of debonding between particles and the binder causes the effective
Young’s modulus to decrease. However, the predicted values of Young’s modulus, in
the presence of debonding, are still higher than experimental data suggesting that there
is considerable debonding between particles and the binder in mock polymer bonder
explosives composed of glass and estane. These results indicate the two-dimensional
finite element simulations that incorporate some amount of damage can be used to obtain
accurate estimates of the effective properties of glass-estane composites and possibly of
polymer bonded explosives with high modulus contrast.

3.2 Introduction

Polymer bonded explosives (PBXs) are extensively used as propellants in solid rocket
motors. These materials are typically viscoelastic particulate composites containing high
volume fractions of explosive particles suspended in a soft binder. For example, PBX
9501 contains about 92% by volume of particles. In addition, the modulus contrast
between particles and the binder in PBX 9501 is around 20,000 at room temperature
and low strain rates. The high modulus contrast between the particles and the binder
as well as the high volume fraction of the particles pose an interesting challenge in the
prediction of effective mechanical properties of PBXs using numerical micromechanics
techniques.

The explosive nature of PBXs makes the experimental determination of their me-
chanical properties hazardous and thus expensive. Mock polymer bonded explosives
containing monodisperse glass beads and an estane binder provide an alternative material
that can be tested extensively and used to provide a basis for validating micromechanics-
based predictions of mechanical properties. Since the effects of high particle volume
fraction and different particle sizes and shapes do not need to be considered for these
glass-estane mock explosives, the evaluation of various micromechanics methods is sim-
pler. The validated micromechanics techniques can then be applied to predict the me-
chanical properties of actual PBXs.
The goal of this investigation is to determine if the initial moduli of a viscoelastic mock PBX composite can be calculated with reasonable accuracy from the initial moduli of the constituents. The finite element method has been used to estimate the effective elastic moduli of glass-estane mock PBXs containing three different volume fractions of glass. First, two-dimensional unit cells containing randomly distributed particles are modeled using finite element analysis and the effect of RVE size on the effective properties is investigated. Three-dimensional finite element analyses are then performed on selected microstructures to determine if there is a significant difference between two-dimensional and three-dimensional estimates. The unit cell based estimates are then compared with third order bounds, differential effective medium estimates, and experimental data. Finally, two-dimensional simulations of the effect of particle debonding on effective elastic moduli are carried out on a selected microstructure, under both tensile and compressive loading.

3.3 Glass-Estane mock PBXs - experimental data

The glass-estane mock PBXs explored in this investigation are composed of spherical soda lime glass beads (650 ± 50 microns) contained in an Estane 5703 binder [7]. The glass beads are linear elastic in the range of conditions used in the experiments and have a density of 2.5 gm/cc, a Young’s modulus of 50,000 MPa, and a Poisson’s ratio of 0.20. Estane 5703 is an elastomeric rubber with a glass transition temperature of -31°C, a melting point of 105°C and a density of 2 g/cc at room temperature. This polymer contains soft and hard segments that enhance entanglement and lead to low temperature flexibility, high temperature stability and good adhesive properties. The elastic properties of Estane 5703 and the glass-estane mocks used in this investigation have been extracted from stress-strain data obtained by Cady et al. [7]. The moduli of Estane 5703 shown in Table 3.1 are for strain rates of 0.001/s and approximately 2400/s and temperatures ranging from -55°C to 23°C. A Poisson’s ratio of 0.49 has been assumed for Estane 5703 under all conditions. The maximum modulus contrast between the glass beads and Estane 5703 is around 10,000.

Initial tangent moduli from compression tests on three glass-estane composites con-
Table 3.1. Young’s modulus of extruded Estane 5703 [7].

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Strain Rate = 0.001/s</th>
<th>Strain Rate ~ 2400/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-40  -30  -20  -5  23</td>
<td>-55  -40  -20  0  22</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>727  267  9.3  7.5  5</td>
<td>6250  4000  2816  2469  2439</td>
</tr>
</tbody>
</table>

Table 3.2. Young’s modulus of composites containing glass and estane [7].

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Strain Rate = 0.001/s</th>
<th>Strain Rate ~ 3500/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-40  -30  -20  20</td>
<td>-40  -20  0  20</td>
</tr>
<tr>
<td>21% Glass</td>
<td>526  600  10  7.5</td>
<td>12000  2353  1412  857</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>833  18.3  11.7  6.7</td>
<td>5600  5600  2693  1539</td>
</tr>
<tr>
<td>44% Glass</td>
<td>833  394  58  28  15</td>
<td>6667  3415  2333  903</td>
</tr>
</tbody>
</table>

 containing 21%, 44% and 59% by volume of glass (25%, 50% and 65% by weight) are shown in Table 3.2. Cady et al. [7] have observed that at low strain rates, there appears to be good bonding between the glass and the estane binder though there are signs of a few debonded particles. However, at high strain rates the binder shows signs of shear damage and there is some damage in the glass. In this investigation, only the effect of particle-binder debonding is simulated. Fracture of the binder or the glass beads is not considered.

3.4 Estimation of elastic moduli

The estimation of effective elastic moduli of a composite using finite elements requires the choice of a unit cell or representative volume element (RVE) that reflects the composition of the composite. The RVE is then subjected to appropriate boundary conditions and the resulting stress-strain field is averaged over the volume of the unit cell.

The average stress and strain fields are assumed to obey the relation
\[ \int_V \sigma_{ij} = C_{ijkl}^{\text{eff}} \int_V \epsilon_{kl} \]  

(3.1)

where \( V \) is the volume of the unit cell, \( \sigma_{ij} \) are the stresses, \( \epsilon_{ij} \) are the strains, and \( C_{ijkl}^{\text{eff}} \) is the effective stiffness tensor of the composite. The effective stiffness tensor can then be calculated using equation 3.1.

An alternative approach for determining the effective orthotropic elastic properties of the unit cell is to compute the boundary forces and displacements produced due to an applied displacement. The two-dimensional Young’s moduli and Poisson’s ratios can then be computed directly using relations such as

\[ E_x = F_x / u_x, \quad \nu_{yx} = -u_y / u_x, \]  

(3.2)

where \( E_x \) is the modulus in the \( x \) direction, \( \nu_{yx} \) is the Poisson’s ratio, \( F_x \) is the reaction force in the \( x \) direction, \( u_x \) is the displacement in the \( x \) direction, and \( u_y \) is the displacement in the \( y \) direction. Equations (3.1) and (3.2) have been found to lead to the same two-dimensional effective elastic properties. A discussion of two- and three-dimensional elastic moduli is given in Appendix A.

Equations (3.1) and (3.2) give two-dimensional elastic moduli for plane strain models. The upper limit on the two-dimensional Poisson’s ratio is 1.0 [31, 84]. These two-dimensional elastic moduli cannot be directly compared with experimentally obtained three-dimensional elastic moduli. In this study, the two-dimensional effective Young’s modulus and Poisson’s ratio in the two orthogonal directions are calculated and then averaged to eliminate directional effects. The assumption is made that a plane-strain analysis of an isotropic material would lead to these average values. The three-dimensional Young’s modulus and Poisson’s ratio are then calculated using the relations [31]

\[ \nu_{\text{eff}} = \nu_{\text{eff}}^{2D} / (1 + \nu_{\text{eff}}^{2D}) \]  

(3.3)

\[ E_{\text{eff}} = E_{\text{eff}}^{2D} [1 - (\nu_{\text{eff}})^2], \]  

(3.4)

where \( \nu_{\text{eff}} \) is the three-dimensional Poisson’s ratio, \( E_{\text{eff}} \) is the three-dimensional Young’s modulus, \( \nu_{\text{eff}}^{2D} \) is the two-dimensional Poisson’s ratio, and \( E_{\text{eff}}^{2D} \) is the two-dimensional Young’s modulus. This approach has been found to give estimates of Young’s modulus.
and Poisson’s ratio that are close to differential effective medium [28] estimates for volume fractions from 0.1 to 0.8 and for modulus contrasts from 10 to 100,000 [85].

3.5 Two-dimensional unit cells

The two-dimensional unit cell chosen for this study was a square box. Circular particles were placed sequentially into randomly selected positions in the unit cell. A small gap was enforced between adjacent particles so that particle-particle contact would not occur. Particles intersecting the boundary of the unit cell were repeated on opposite boundaries for periodicity of the unit cell.

The three glass-estane composites (21%, 44%, and 59% by volume of glass) were each modeled using five unit cells of increasing size that contain 5, 10, 20, 50, and 100 particles. Five different particle distributions were generated for each combination of volume fraction and number of particles in the unit cell (25 distributions for each of the three composites). Five particle distributions for each of the three glass-estane composites are shown in Figure 3.1.

In this study, the finite element analysis package ANSYS [86] was used to simulate the various microstructures. A plane strain assumption was used for the two-dimensional analyses. Displacement boundary conditions were applied along one boundary and the nodes along the orthogonal boundary were coupled to move together as shown in Figure 3.2. Periodicity of displacement boundary conditions was enforced along parallel edges of the unit cell.

The glass beads (particles) and the estane binder were modeled as isotropic, linear elastic materials. Six-noded, displacement-based, plane strain triangles were used to discretize the geometry of the two-dimensional unit cells used in this study. Bathe [87] has suggested the use of nine-noded mixed displacement-pressure (9-3 u/p) elements to model nearly incompressible materials such as estane. An investigation into the effect of using 9-3 u/p elements to model the rubbery binder has found that the use of such elements does not significantly affect the effective elastic moduli (compared to moduli obtained using six-noded displacement-based triangles). A further investigation into the effect of the constitutive law for the binder on the effective properties was
Figure 3.1. Sample particle distributions and unit cells of various sizes containing 21%, 44% and 59% by volume of monodisperse circular particles. Note that the size of the unit cell increases as the number of particles increases.

Figure 3.2. Displacement boundary conditions used to calculate the stress-strain behavior of a unit cell. A uniform displacement is applied in the $x$-direction to nodes 3, 6 and 9. The orthogonal $y$-direction displacement at nodes 7, 8 and 9 are coupled so that these nodes move together.
performed using a plane strain Mooney-Rivlin rubber model for the estane binder. Non-linear analyses using the Mooney-Rivlin rubber model were found to generate stresses and strains similar to those using a linear elastic model. These results suggest that linear elastic displacement-based elements provide a reasonably accurate representation of glass-estane composites.

### 3.5.1 Effect of unit cell size

To determine the effect of unit cell size on the effective elastic properties, two-dimensional finite element simulations were performed on particle distributions representing glass-estane mock PBXs (as shown in Figure 3.1). The arithmetic mean of the effective Young’s modulus and Poisson’s ratio has been calculated for five model particle distributions at each combination of volume fraction and unit cell size. Properties of glass and estane at room temperature and at a strain rate of 0.001/s were used in the simulations.

Figures 3.3(a) and 3.3(b) show the variation of effective Young’s modulus and Poisson’s ratio with unit cell size for the glass-estane composites with three volume fractions of glass. For the composite containing 21% glass, Figure 3.3(a) shows that the predicted

![Figure 3.3](image-url)

**Figure 3.3.** Variation of effective elastic properties with the size of the unit cell for a strain rate of 0.001/s and at a temperature of 23ºC.
effective Young’s modulus is almost constant, both among the five models at a particular unit cell size and between different unit cell sizes. The range of variation of the effective Poisson’s ratio, shown in Figure 3.3(b), is also negligible for these particle distributions.

For the glass-estane composite containing 44% glass, the Young’s modulus (Figure 3.3(a)) does not vary much with unit cell size. Variations between different particle distributions at the same unit cell size are also negligible. Though the average effective Poisson’s ratio (Figure 3.3(b)) remains relatively constant with unit cell size, there is some variation between particle distributions, especially at smaller unit cell sizes.

The effective Young’s modulus for a composite containing 59% glass is also shown in Figure 3.3(a). In this case, the mean effective modulus varies slightly for the smaller unit cells. The variation between unit cell sizes becomes negligible for unit cells containing 10 particles or more (≥ 2.4 mm). Additionally, large variations occur between particle distributions for small unit cell sizes. The variation becomes smaller for unit cells containing 50 particles or more (≥ 5 mm). Similar trends are observed for the effective Poisson’s ratio shown in Figure 3.3(b). At small unit cell sizes, the variation between particle distributions is large but the mean effective Poisson’s ratio stabilizes at unit cell sizes greater than 5 mm.

Results shown in Figure 3.3 indicate that the size of the two-dimensional unit cell required to calculate the effective properties of monodisperse random composites containing circular particles is quite small. For the three volume fractions investigated, the smallest unit cell that can be used is around 4 mm in size or around six particle diameters. Results in Figure 3.3 also show that the calculation of the effective Poisson’s ratio requires a larger unit cell size than that for the effective Young’s modulus. A unit cell size of around 5 mm (7.5 particle diameters) is adequate for all the volume fractions modeled. For unit cells containing 21% and 44% by volume of particles, an even smaller unit cell size can be chosen to calculate the effective Poisson’s ratio. In general, a unit cell that is 6 to 7 particle diameters in size (or containing 10 to 20 particles) appears to be optimal for the calculation of effective properties of low volume fraction composites containing monodisperse circular particles.
3.6 Three-dimensional unit cells

Two-dimensional unit cells were used in this investigation primarily because detailed three-dimensional microstructures are difficult to generate and mesh so that they are computationally intensive. The process of generating particle distributions becomes nontrivial for microstructures containing more than 45% by volume of monodisperse spheres. Beyond these concentrations, even if random particle distributions can be generated, the particles are so close to each other that extremely thin elements are required to mesh the regions between particles. Since the number of elements required to discretize three-dimensional models is significantly larger than that for corresponding two-dimensional models, large computational resources are necessary for three-dimensional models. However, comparisons with three-dimensional simulations are necessary to determine if two-dimensional models adequately represent three-dimensional materials such as glass-estane composites.

To address this issue, two-dimensional finite element simulations were compared with three-dimensional finite element simulations for unit cells containing 21% and 44% spheres by volume. The three-dimensional unit cells were generated such that the length of each side was the same as that for the corresponding two-dimensional unit cell containing 10 particles. The unit cells were approximately 4 mm and 2.7 mm in size for the composites containing 21% glass and 44% glass, respectively. The two three-dimensional unit cells are shown in Figure 3.4(a). Each of these unit cells was divided into five equal slices using dividing planes perpendicular to one direction. One such slice for each unit cell is shown in Figure 3.4(b).

Due to computational limitations, finite element simulations were performed on these slices instead of the complete unit cell. Ten-noded tetrahedral elements were used to discretize the geometry of the slices. Displacement boundary conditions similar to those shown in Figure 3.2 were applied to each plane of nodes along the thickness of a slice. Boundary nodes on the plane of the slice were coupled in the out of plane direction. The effective properties of the three-dimensional unit cells were calculated using equations (3.1).
Figure 3.4. Three-dimensional unit cells containing 21% and 44% by volume of monodisperse circular particles and slices from the unit cells used for three-dimensional simulations.
Figure 3.5(a) shows the effective Young’s modulus computed using two-dimensional and three-dimensional unit cells for 21% glass. Figure 3.5(b) shows the two- and three-dimensional unit cell based Young’s modulus for 44% glass. These estimates are for a strain rate of 0.001/s. The two- and three-dimensional predictions of Young’s modulus do not differ significantly from each other. It is also observed that the three-dimensional estimates are always slightly higher than the corresponding two-dimensional estimates. The difference between the two- and three-dimensional estimates is observed to increase with increase in glass volume fraction. Similar results have been obtained for the Poisson’s ratio, in which case the difference between two- and three-dimensional calculations is even smaller. Since the differences between the two are small, the two-dimensional finite element calculations are considered sufficiently accurate for the purposes of this work.

![Graph](image)

**Figure 3.5.** Young’s modulus of glass-estane composites from two-dimensional and three-dimensional unit cell based finite element calculations. The estimates are for a strain rate of 0.001/s.
3.7 Comparison of estimates and experimental data

In this section, effective Young’s moduli from two-dimensional finite element (FEM) calculations are compared with third-order bounds [23] and experimental data. The finite element calculations were performed on unit cells of size approximately 9 mm, 6 mm, and 5 mm for glass-estane composites containing 21%, 44%, and 55% glass by volume, respectively (50 particles in each unit cell).

The calculation of third-order bounds requires knowledge of two geometric parameters $\zeta_p$ and $\eta_p$ in addition to the volume fractions $f_p$ and $f_b$ of the particles and the binder. For two-component composites containing monodisperse non-overlapping spheres, these parameters are given by [84]

$$
\zeta_p = \begin{cases} 
0.21068 f_p - 0.04693 f_p^2 & \text{for } f_p \leq 0.54, \\
0.21068 f_p & \text{for } 0.54 \leq f_p \leq 0.6,
end{cases} \tag{3.5}
$$

$$
\eta_p = 0.48274 f_p \tag{3.6}
$$

The third-order bounds on the Young’s modulus have been calculated after determining $\zeta_p$ and $\eta_p$ for the three volume fractions of glass.

Figure 3.6(a) shows the experimentally determined Young’s moduli, the finite element estimates, and third-order bounds at a strain rate of 0.001/s for a glass-estane composite containing 21% glass beads by volume. At low strain rate and ambient temperatures, there is a considerable difference between the upper and lower bounds. However, at low temperatures close to the glass transition temperature of estane, the stiffening of estane leads to smaller modulus contrast between glass and estane and the bounds are considerably closer. The finite element (FEM) estimates almost coincide with the lower bounds for this volume fraction of glass. Most of the experimental Young’s moduli lie below the lower bounds.

Figure 3.6(b) shows the results for a strain rate of approximately 2400/s. The high strain rate experimental data for the composites are at a strain rate of approximately 3500/s which is higher than the strain rate used to experimentally determine properties of Estane 5703 (approximately 2400/s strain rate). It is assumed that composite properties do not vary considerably at high strain rates and that the experimental data for the glass-estane composites at a strain rate of approximately 3500/s can be compared with
Figure 3.6. Comparison of experimental Young’s modulus, bounds and FEM calculations for glass-estane composites containing 21% by volume of monodisperse glass beads.

predicted values from finite element analyses for a strain rate of approximately 2400/s. From the high strain rate data shown in Figure 3.6(b) it can be observed that the bounds are quite close to each other. This is because of the relatively low modulus contrast between glass and estane at these strain rates. The experimental data are again observed to be considerably lower than the lower bounds except at a temperature of -40° C in which case the experimental value of Young’s modulus is two times the finite element estimate and higher than the upper bound.

Figure 3.7(a) shows the experimental data, bounds, and finite element estimates of Young’s moduli for a glass-estane composite containing 44% by volume of glass at a strain rate of 0.001/s. In this case, the finite element estimates are 1.5 to 2 times higher than the lower bounds. However, the experimental data are almost an order of magnitude lower than the finite element estimates. Figure 3.7(b) shows the experimental and predicted Young’s moduli at a strain rate of 2400/s. The bounds are quite close to each other and the finite element estimates are slightly higher than the lower bounds, but the experimental data are considerably lower than the lower bounds. The finite element
Figure 3.7. Comparison of experimental Young’s modulus, bounds and FEM calculations for glass-estane composites containing 44% by volume of monodisperse glass beads.

estimates always lie within the third-order bounds.

Results for the glass-estane composite containing 59% by volume of glass are shown in Figures 3.8(a) and 3.8(b). The finite element estimates are higher than the lower bound. The difference between the estimate and the lower bound is larger than for composites with lower volume fractions of glass. At a strain rate of 0.001/s, the experimental data are quite close to the lower bound near room temperature. However, near the glass transition temperature of estane, the experimental Young’s modulus is an order of magnitude lower than the finite element estimate and the lower bound. At high strain rates and low temperatures, the difference between finite element predictions and experimental data is less pronounced. However, at high temperatures and high strain rates there is almost an order of magnitude difference between predictions and experiment.

The fact that the experimental data are lower than the bounds may indicate that there is considerable debonding of glass-beads from the estane binder. The comparisons between the finite element predictions and experimental data also suggest the assumption of perfect bonding between the glass and the binder is inaccurate. Micrographs of
glass-estane composites also show that there is some debonding at low strain rates [7]. Damage in the composite appears to play a considerable role in determining effective elastic properties. This damage can be in the form of glass-binder debonds/dewetting, cracking of glass beads or cracking of the binder. Such damage has been observed in glass-estane mock PBXs by Cady [7]. The effect of particle debonding on the effective properties is investigated in the next section. The goal is to determine if debonding is adequate to explain the observed discrepancy between finite element estimates and experimentally determined properties of glass-estane composites.

The high strain rate data on Estane 5703 and the glass-estane mock explosives have been determined using stress-strain curves from split Hopkinson pressure bar impact tests. In these tests, the elastic wave moving through a test specimen reaches equilibrium some time after the specimen is impacted. Hence, the initial region of the stress-strain curve may not accurately represent the actual response of the material at small strains. This may be one of the reasons for the high estimates of modulus at high strain rates from finite element simulations. It is also possible that unless the loading history is taken
into consideration, the effective initial moduli of viscoelastic composites at various strain rates and temperatures cannot be predicted accurately.

### 3.8 Effect of particle debonding

Two-dimensional finite element simulations were performed on the microstructure shown in Figures 3.9(a) and 3.9(b) to investigate the effect of particle debonding on effective properties. This microstructure represents a glass-estane composite containing 44% glass by volume. Six of the particles in the microstructure are completely contained in the unit cell while the remaining four intersect the boundary.

The first set of simulations involved selecting one of the six completely contained particles and completely dissociating it from the surrounding material to simulate a debonded particle. The remainder of the geometry of the unit cell was meshed using six-noded triangles and the debonded particle was meshed separately. Next, two nodes on diametrically opposite sides of the debonded particle were coupled to the corresponding nodes in the adjacent mesh. The locations of these nodes were chosen so that the line joining the two nodes was perpendicular to the direction of the applied strain.

![Figure 3.9](image)

**Figure 3.9.** Debonded particles under (a) compression and (b) tension for a glass-estane composite containing 44% by volume of monodisperse glass beads with three debonded particles. Displacements shown are three times the actual. The applied strain is 1%.
load. Contact elements were created at the hole in the unit cell and at the boundary of the debonded particle. A nonlinear contact simulation was performed on the unit cell with displacement boundary conditions similar to those shown in Figure 3.2. A uniform inward displacement along a boundary was used to simulate compression while a uniform outward displacement was used to simulate tension. The resulting boundary forces and displacements at equilibrium were used in equations (3.2) to compute the effective Young’s modulus and Poisson’s ratio of the unit cell. The above procedure was repeated five times, with a different particle being debonded from the surrounding material in each simulation. This process was repeated with two, three, four and five debonded particles. Finally, one additional simulation was performed with all six particles debonded from the surrounding material.

The deformed shape of a unit cell with three debonded particles under a compressive load is shown in Figure 3.9(a). Figure 3.9(b) shows the deformed shape of the same unit cell under a tensile load. The amount of separation of particles and binder is greater in tension than under compression. The orientation of the gap between the particles and the binder is not always aligned with the direction of applied load and can be affected considerably by the location of adjacent particles.

For each simulation, displacements simulating compression were applied first in the $x$ direction and then in the $y$ direction. The effective Young’s moduli in the two directions were averaged to eliminate directional effects. The change in effective compressive Young’s modulus with increasing particle debonding can be observed in Figure 3.10(a). The corresponding change in the tensile Young’s modulus is shown in Figure 3.10(b). The data points shown in the figure represent the arithmetic mean of the effective moduli predicted for the different combinations of debonded particles at each level of debonding. The standard deviation for each data point is around 10% of the mean. The effective Young’s modulus decreases with increasing particle-binder debond. However, under compression, even when 6 of the 10 particles (60% of the particles) have debonded, the effective properties predicted by finite element simulations are still higher than the experimentally determined properties. At the small strains that have been applied (around 1%), it is unlikely that such a high percentage of particles debond in the actual material.
Figure 3.10. Effect of particle debonding on predicted values of Young’s modulus of 44% glass/56% estane composite (a) under compression (b) under tension. ▼ = Expt. (compression); ——— = FEM - fully bonded; ○ = FEM - one particle debonded; △ = FEM - two particles debonded; * = FEM - three particles debonded; ———— = FEM - four particles debonded; —·—— = FEM - five particles debonded; ······· = FEM - all six particles debonded.
The high strain rate results show the same qualitative effects as the low strain rate results. The tensile modulus decreases more rapidly with increasing debond than the compressive modulus. The compressive and tensile moduli can be considerably different for glass-estane mock PBXs in the presence of debonded particles. Experimental data from tension tests are necessary to validate the tension-based simulations.

### 3.9 Summary and conclusions

Experimental data on the Young’s moduli of extruded Estane 5703 and glass-estane mock polymer bonded explosives show strong dependence on temperature and strain rate. Two-dimensional finite element simulations based on a unit cell have been performed to determine if the initial modulus of the components of a viscoelastic, glass-estane mock polymer bonded explosive can be used to predict the effective initial modulus of the composite. A number of different unit cell sizes were simulated in order to determine appropriate unit cells for the glass-estane composites containing three different volume fractions of glass. It has been found that, in two dimensions, unit cells containing five to ten equal sized particles are adequate for the prediction of elastic moduli. A number of three-dimensional particle distributions have also been simulated using finite elements. The three-dimensional models predict moduli that are around 5% to 10% higher than the two-dimensional models. It can be concluded that two-dimensional plane strain models estimate elastic moduli of glass-estane mock explosives as accurately as three-dimensional models.

Rigorous third-order bounds on the effective elastic properties of the glass-estane composites show that the experimental data are close to the lower bounds at low strain rates. This finding suggests that third-order lower bounds provide excellent approximations to the effective Young’s modulus of low volume fraction composites with high modulus contrast at low strain rates. However, at high strain rates, except at temperatures close to the glass transition temperature of estane, the experimental moduli are considerably lower than the predicted Young’s moduli. This finding suggests that there may be substantial debonding and particle/binder fracture in the composites when high strain rate loads are applied.
Two-dimensional finite element simulations of various glass-estane composite particle distributions also show that the predicted elastic moduli are considerably higher than the experimentally determined values. This result suggests that there may be particle-binder debonding in the glass-estane composites. Simulations performed on a model glass-estane particle distribution with increasing particle debonding have shown that increased debonding decreases the effective modulus of the composite. However, even when 60% of the particles have debonded from the surrounding material, the predicted effective moduli are higher than the experimental values. It is unlikely that such a high percentage of the particles would have debonded under the applied strain of around 1%. Therefore, particle debonding cannot fully explain the high moduli obtained from finite element simulations.
CHAPTER 4

EFFECTIVE ELASTIC MODULI OF POLYMER BONDED EXPLOSIVES FROM FINITE ELEMENT SIMULATIONS

4.1 Abstract

Finite element analysis has been used successfully to estimate the effective properties of many types of composites. The prediction of effective elastic moduli of polymer-bonded explosives provides a new challenge. These particulate composites contain extremely high volume fractions of explosive particles (> 0.9). At room temperature and higher, the Young’s modulus of the particles can be 20,000 times that of the binder. Under these conditions, rigorous bounds and analytical approximations for effective elastic properties predict values that are orders of magnitude different from the experimental values. In this work, an approach is presented that can be used to predict three-dimensional effective elastic moduli from two-dimensional finite element simulations. The approach is validated by comparison with differential effective medium estimates and three-dimensional finite element simulations. The two-dimensional finite element approach has been used to determine the properties of models of polymer bonded explosives and PBX 9501 in particular, containing high volume fractions of circular and square particles with high modulus contrasts. Results show that estimates of effective elastic properties from two-dimensional finite element calculations are close to the values predicted by the differential effective medium approach for a large range of volume fractions and modulus contrasts. Two- and three-dimensional finite element estimates for volume fractions from 0.7 to 0.9 and found not to differ considerably. Simulations of models of polymer bonded explosives and PBX 9501 show that the microstructure, the amount of discretization, and the type of element used play a considerable role.
in determining the value predicted by finite element simulations. The effective elastic moduli of PBX 9501 predicted by finite element calculations can vary from 200 MPa to 10,000 MPa depending on the microstructure and level of discretization used. The results also suggest that if a microstructure can be found that accurately predicts the elastic properties of PBX 9501 at a certain temperature and strain rate, then the same microstructure can be used to predict elastic properties at other temperatures and strain rates.

4.2 Introduction

Experimental determination of the mechanical properties of polymer-bonded explosives (PBXs) is hazardous and highly expensive. An alternative to experimentation is the numerical determination of material properties using finite element analysis. PBXs are particulate composites containing explosive particles and a rubbery binder. The particle size distributions in these materials and the mechanical properties of the constituents are required for finite element simulations of the microstructure of these materials. The mechanical properties of the explosive particles can be determined from molecular dynamics simulations. The rubbery binder is amenable to mechanical testing and properties can be determined from laboratory tests. The goal of this work is to investigate if the elastic properties of PBXs can be determined using finite element analyses of PBX microstructures.

The major challenges involved in finite element modeling of PBXs are the high volume fraction of particles in PBXs ($f_p > 0.90$) and the high modulus contrast between particles and binder ($E_p/E_b = 10,000$ to $20,000$) at and above room temperature and at low strain rates. Because of the high volume fractions, microstructures are difficult to generate and even more difficult to digitize from micrographs. Three-dimensional finite element models of these materials require considerable computational power. The high modulus contrast leads to large stress concentrations at the interface of particles and the binder. These stress concentrations cannot be simulated adequately without a high degree of mesh discretization. However, detailed numerical simulations are required for the prediction of effective properties of PBXs because rigorous bounds and analytical
approaches predict values of elastic modulus that are orders of magnitude different from the experimental values.

In this work, a procedure is outlined whereby two-dimensional finite element simulations can be used to estimate the three-dimensional elastic moduli. Finite element estimates on unit cells containing circular particles are compared with differential effective medium estimates of effective elastic moduli for a wide range of volume fractions and modulus contrasts. Two-dimensional finite element estimates for selected microstructures are then compared to three-dimensional estimates for particle volume fractions of 0.7, 0.75 and 0.8.

An appropriate model of PBX 9501 is determined from simulations of manually generated and randomly generated microstructures based on the particle size distribution of PBX 9501. Finite element calculations are then performed on this model to estimate the elastic moduli of PBX 9501 for various temperatures and strain rates.

### 4.3 Finite element approach

Numerical determination of the effective properties of particulate composites involves the calculation of the stress and strain fields for a representative volume element (RVE) that simulates the microstructure of the composite. These stresses and strains are averaged over the volume (V) of the RVE and the effective elastic stiffness tensor $C_{ijkl}^{\text{eff}}$ of the composite can be calculated from the tensor relation

$$
\int_V \sigma_{ij} dV = C_{ijkl}^{\text{eff}} \int_V \epsilon_{kl} dV,
$$

where $\sigma_{ij}$ are the stresses and $\epsilon_{ij}$ are the strains. The bulk mechanical response of a random composite is isotropic. However, the size of a RVE than can be simulated numerically is necessarily much smaller than the bulk and may not be isotropic. In this work, it is assumed that the deviation from isotropy of an RVE is small. The stress-strain relation for the RVE can be written in Voigt notation as

$$
\begin{bmatrix}
\langle \sigma_{11} \rangle_V \\
\langle \sigma_{22} \rangle_V \\
\langle \sigma_{33} \rangle_V \\
\langle \sigma_{23} \rangle_V \\
\langle \sigma_{31} \rangle_V \\
\langle \sigma_{12} \rangle_V \\
\end{bmatrix}
= 
\begin{bmatrix}
C_{11}^{\text{eff}} & C_{12}^{\text{eff}} & C_{13}^{\text{eff}} & 0 & 0 & 0 \\
C_{12}^{\text{eff}} & C_{22}^{\text{eff}} & C_{23}^{\text{eff}} & 0 & 0 & 0 \\
C_{13}^{\text{eff}} & C_{23}^{\text{eff}} & C_{33}^{\text{eff}} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44}^{\text{eff}} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55}^{\text{eff}} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}^{\text{eff}} \\
\end{bmatrix}
\begin{bmatrix}
\langle \epsilon_{11} \rangle_V \\
\langle \epsilon_{22} \rangle_V \\
\langle \epsilon_{33} \rangle_V \\
\langle \epsilon_{23} \rangle_V \\
\langle \epsilon_{31} \rangle_V \\
\langle \epsilon_{12} \rangle_V \\
\end{bmatrix}
$$

(4.2)
where \( \langle a \rangle_V \) is the volume average of the quantity \( a \). Equation (4.2) can also be inverted and written in terms of the directional Young’s moduli, Poisson’s ratios and shear moduli as

\[
\begin{bmatrix}
\langle \varepsilon_{11} \rangle_V \\
\langle \varepsilon_{22} \rangle_V \\
\langle \varepsilon_{33} \rangle_V \\
2 \langle \varepsilon_{23} \rangle_V \\
2 \langle \varepsilon_{31} \rangle_V \\
2 \langle \varepsilon_{12} \rangle_V
\end{bmatrix}
= 
\begin{bmatrix}
1/E_{11}^{\text{eff}} & -\nu_{12}^{\text{eff}}/E_{11}^{\text{eff}} & -\nu_{13}^{\text{eff}}/E_{11}^{\text{eff}} & 0 & 0 & 0 \\
-\nu_{12}^{\text{eff}}/E_{22}^{\text{eff}} & 1/E_{22}^{\text{eff}} & -\nu_{23}^{\text{eff}}/E_{22}^{\text{eff}} & 0 & 0 & 0 \\
-\nu_{13}^{\text{eff}}/E_{33}^{\text{eff}} & -\nu_{23}^{\text{eff}}/E_{33}^{\text{eff}} & 1/E_{33}^{\text{eff}} & 0 & 0 & 0 \\
0 & 0 & 0 & 1/G_{23}^{\text{eff}} & 0 & 0 \\
0 & 0 & 0 & 0 & 1/G_{31}^{\text{eff}} & 0 \\
0 & 0 & 0 & 0 & 0 & 1/G_{12}^{\text{eff}}
\end{bmatrix}
\begin{bmatrix}
\langle \sigma_{11} \rangle_V \\
\langle \sigma_{22} \rangle_V \\
\langle \sigma_{33} \rangle_V \\
\langle \sigma_{23} \rangle_V \\
\langle \sigma_{31} \rangle_V \\
\langle \sigma_{12} \rangle_V
\end{bmatrix}
\]

(4.3)

where the directional Young’s moduli \( E_{11}^{\text{eff}}, E_{22}^{\text{eff}}, \) and \( E_{33}^{\text{eff}} \) differ by a small amount from the isotropic Young’s modulus \( E_{\text{eff}} \). Similarly, the mean of the Poisson’s ratios \( \nu_{12}^{\text{eff}}, \nu_{23}^{\text{eff}}, \nu_{13}^{\text{eff}}, \nu_{23}^{\text{eff}}, \nu_{23}^{\text{eff}}, \) and \( \nu_{32}^{\text{eff}} \) is assumed to be close to the isotropic Poisson’s ratio \( \nu_{\text{eff}} \) and the mean of the shear moduli \( G_{12}^{\text{eff}}, G_{23}^{\text{eff}}, \) and \( G_{31}^{\text{eff}} \) is assumed to be close to the isotropic shear modulus \( G_{\text{eff}} \).

The determination of effective isotropic elastic modulus of particulate composites using three-dimensional finite element analysis therefore requires the determination of volume averaged stresses and strains under appropriate boundary conditions. Once these stresses and strains are known for an RVE, equation (4.3) can be used to determine the effective elastic moduli of the RVE. An investigation into effects of boundary conditions revealed a uniaxial state of stress develops in a RVE when a uniform boundary displacement is applied in one direction and periodicity of boundary displacements is maintained. This means that the effective Young’s modulus and Poisson’s ratio in a particular direction can be directly computed from equation (4.3) by applying a uniform displacement in that direction. The effective isotropic Young’s modulus and Poisson’s ratio can then be calculated by averaging the values obtained in the three orthogonal directions from three simulations. The effective shear modulus can be calculated directly from the effective isotropic Young’s modulus and Poisson’s ratio.

The estimation of effective elastic properties from three-dimensional simulations is straightforward in principle. However, not only is it difficult to generate RVEs containing high volume fractions of random spherical particles, meshing such three-dimensional RVEs is nontrivial. Even if RVEs can be generated and meshed, solution of the finite
element system of equations can be prohibitive in terms of computational expense. A
two-dimensional approach is described below that requires relatively little computa-
tional expense. This approach can be used to arrive at reasonable estimates of three-
dimensional effective properties of particulate composites.

In the two-dimensional simulations of particulate composites performed in this study,
a cross-section of the composite is chosen that contains the same area fraction of parti-
cles as the volume fraction of particles in the composite. Finite element analyses are
then performed on this square RVE assuming a state of plane strain. The stress-strain
equation (4.3) can be written in planar or two-dimensional form as

\[
\begin{bmatrix}
\langle \epsilon_{11} \rangle_v \\
\langle \epsilon_{22} \rangle_v \\
2 \langle \epsilon_{12} \rangle_v
\end{bmatrix}
= \begin{bmatrix}
1/E_{11}^{\text{eff}} & -\nu_{12}^{\text{eff}} / E_{11}^{\text{eff}} & 0 \\
-\nu_{12}^{\text{eff}} / E_{22}^{\text{eff}} & 1/E_{22}^{\text{eff}} & 0 \\
0 & 0 & 1/G_{12}^{\text{eff}}
\end{bmatrix}
\begin{bmatrix}
\langle \sigma_{11} \rangle_v \\
\langle \sigma_{22} \rangle_v \\
\langle \sigma_{12} \rangle_v
\end{bmatrix}
\tag{4.4}
\]

where \( E_{11}^{\text{eff}}, E_{22}^{\text{eff}}, \nu_{12}^{\text{eff}}, \) and \( \nu_{12}^{\text{eff}} \) are two-dimensional Young’s moduli and Poisson’s ratios
and different from their three-dimensional counterparts. A brief explanation of two-
dimensional elastic moduli is given in Appendix A. Uniform displacements are applied
to the ‘1’ and ‘2’ directions of the RVE and periodic displacements are enforced along
the remainder of the boundary to arrive at uniaxial average stresses and the corresponding
average strains in the RVE. The effective moduli are calculated using equation (4.4) and
the directional moduli are averaged to arrive at a mean effective Young’s modulus \( E_{\text{eff}}^{2D} \)
and a mean effective Poisson’s ratio \( \nu_{\text{eff}}^{2D} \) for the RVE. These moduli can also be thought
of as effective transverse moduli of a composite containing unidirectional cylinders.

It is assumed that these transverse moduli are equal to the two-dimensional apparent
moduli of an isotropic, homogeneous material subjected to plane strain. Since equation
(4.4) is a two-dimensional stress-strain law, the two-dimensional moduli have to be
converted to three-dimensional moduli using the relations [31]

\[
\nu_{\text{eff}} = \frac{\nu_{\text{eff}}^{2D} / (1 + \nu_{\text{eff}}^{2D})}{1 - (\nu_{\text{eff}}^{2D})^2},
\tag{4.5}
\]

\[
E_{\text{eff}} = \frac{E_{\text{eff}}^{2D} / (1 + \nu_{\text{eff}}^{2D})}{1 - (\nu_{\text{eff}}^{2D})^2},
\tag{4.6}
\]

where \( \nu_{\text{eff}} \) is the effective Poisson’s ratio in three dimensions and \( E_{\text{eff}} \) is the three-
dimensional effective Young’s modulus.
4.4 Validation of approach

To determine if the two-dimensional finite element simulation approach provides reasonable estimates of three-dimensional effective elastic properties of particulate composites, finite element analyses were performed on the two-dimensional RVEs containing 10% to 92% by volume of circular particles that are shown in Figure 4.1. The circular particles were placed sequentially at random locations in each RVE such that no two particles were in contact. The particle size distribution in each RVE was based on distributions of the dry blend of PBX 9501 [17]. The Young’s modulus of the particles in these finite element simulations was 100,000 MPa and the Poisson’s ratio was 0.2. The Young’s modulus of the binder was varied from 1 MPa to 10,000 MPa in multiples of 10. The binder Poisson’s ratio was chosen to be 0.49. The effective properties predicted using the finite element analyses were compared with differential effective medium estimates [29, 28]. The differential effective medium approach has been found to provide excellent estimates of elastic properties of particulate composites [28].

Figure 4.2(a) shows effective three-dimensional Young’s moduli from finite element (FEM) and differential effective medium (DEM) calculations. Figure 4.2(b) shows the corresponding three-dimensional Poisson’s ratios. The solid lines in the figures are lines of constant modulus contrast between particles and binder and represent the effective elastic property calculated using DEM. The finite element results are shown as squares. The finite element and the DEM predictions are shown to agree remarkably well for all modulus contrasts and for all the simulated volume fractions of particles, implying that the approach described in the previous section gives reasonable estimates of effective elastic properties over a considerable range of volume fractions and modulus contrasts.

To obtain a more direct estimate of the effectiveness of the two-dimensional models, a second set of finite element simulations was performed on square and cubic RVEs containing particle volume fractions of 0.7, 0.75, and 0.8. The two-dimensional RVEs are shown in Figure 4.3(a) and the three-dimensional RVEs are shown in Figure 4.3(b).
Figure 4.1. RVEs containing 10% to 92% by volume of circular particles. $f_p$ is the volume fraction of particles in a RVE.

Figure 4.2. Comparison of finite element (FEM) and differential effective medium (DEM) predictions. $E_b$ is the Young’s modulus of the binder.
Figure 4.3. Two- and three-dimensional RVEs containing 70%, 75% and 80% particles by volume. $f_p$ is the volume fraction of particles.
For the two-dimensional simulations, each RVE was discretized using six-noded triangles and approximately 60,000 nodes. Displacement boundary conditions were applied and the average stresses and strain were used to calculate two-dimensional effective Young’s moduli and Poisson’s ratios. The two-dimensional moduli were then converted into three-dimensional moduli using the approach described in the previous section. The three-dimensional RVEs were discretized using 10-noded tetrahedral elements with a total of around 100,000 nodes. A uniform displacement was applied perpendicular to one of the faces while the remaining faces were constrained to displace periodically. The three-dimensional Young’s modulus and Poisson’s ratio were directly calculated from the average stresses and strains for these three-dimensional models.

Figure 4.4(a) shows the effective Young’s modulus calculated using the two- and three-dimensional RVEs shown in Figure 4.3. The Young’s modulus used for the particles was 15,300 MPa and the Poisson’s ratio was 0.32. The Young’s modulus of the binder was 0.7 MPa and the Poisson’s ratio was 0.49. These values correspond to the moduli of HMX and the binder of PBX 9501 at room temperature and low strain rate [14, 8]. Though the three-dimensional models predict higher values of Young’s modulus than the two-dimensional models, the difference between the two- and three-dimensional estimates of Young’s modulus is small when compared to the modulus contrast between the particles and the binder. Figure 4.4(b) shows the effective Poisson’s ratio for the two- and three-dimensional finite element models. The three-dimensional models predict slightly lower values of Poisson’s ratio than the two-dimensional models. Both two- and three-dimensional models predict a sharp decrease in Poisson’s ratio with increasing particle volume fraction.

Comparisons of the two-dimensional finite element approach with differential effective medium approximations and three-dimensional finite element models suggest that two-dimensional analyses provide reasonable approximations of effective properties of particulate composites. Hence, two-dimensional models have been used to estimate the effective properties of PBX 9501 in the remainder of this work.
Figure 4.4. Two- and three-dimensional estimates of effective Young’s modulus and Poisson’s ratio.

4.5 Modeling polymer bonded explosives

Most micromechanical calculations for PBXs have been carried out using subgrid models that use highly simplified models of the microstructure (for example, spherical grains coated with binder or spherical voids in an effective PBX material [88]). Closed form solutions from these simple models have been used to provide properties for macroscopic simulations. More detailed calculations have used microstructures containing ordered arrays of circles or polygons in two or three dimensions to model PBXs [52, 89]. These models do not reflect the microstructure of PBXs and hence have limited use for predicting thermoelastic properties. Better two-dimensional approximations of the microstructure have been constructed from digital images of the material and used by Benson and Conley [90] to study some aspects of the micromechanics of PBXs. However, such microstructures are extremely difficult to generate and require state-of-the-art image processing techniques and excellent images to accurately capture details of the geometry of PBXs. More recently Baer [91] has used a combination of Monte Carlo and molecular dynamics techniques to generate three-dimensional microstructures containing spheres and oriented cubes that appear to represent PBX microstructures well. However, the generation of a single realization of these microstructures is very time
consuming and often leads to a maximum packing fraction of about 70%. Periodicity is also extremely difficult to maintain in the RVEs generated by this method.

Both manually and automatically generated two-dimensional RVEs of PBX 9501 are discussed in this section. The effective elastic moduli of these RVEs from finite element calculations are then compared with experimentally determined moduli of PBX 9501. As in the previous section, the particles in the RVEs represent HMX and have a Young’s modulus of 15,300 MPa and a Poisson’s ratio of 0.32 [14] and the binder has a Young’s modulus of 0.7 MPa and a Poisson’s ratio of 0.49 [8]. The effective properties computed from these component properties are compared with the Young’s modulus of 1,013 MPa and Poisson’s ratio of 0.35 [8] of PBX 9501.

4.5.1 Manually generated microstructures

Figure 4.5 shows six two-dimensional microstructures representing PBX 9501. Each RVE is filled with particles of various sizes since PBXs are typically a mixture of coarse and fine grains with the finer grains forming a filler between coarser grains. The volume fractions of particles in each of these models is 90±0.5%. All the models possess square symmetry. The RVEs have also been designed so that particle-particle contact is avoided. Finite element simulations were performed on these RVEs using six-noded triangular elements such that the geometry of the circular particles was represented accurately. The approach discussed in Section 4.3 was used to determine the effective Young’s modulus and Poisson’s ratios of these RVEs.

Table 4.1 shows the effective Young’s modulus and Poisson’s ratios of the six RVEs. The values of the effective Young’s modulus range from 42 MPa to 192 MPa, with a mean of 132 MPa and a standard deviation of 54 MPa. In comparison, the Young’s modulus of PBX 9501 is 1,013 MPa; around 500% to 800% of that predicted using the six RVEs. Among the six RVEs, the Young’s modulus appears to be higher for the models with lower amounts of binder along the edges of the RVE. Models 1 through 3 have a single large particle and many smaller particles and show approximately the same effective behavior. Model 4, with a smaller ratio between the radius of the largest and the smallest particles, has a lower effective Young’s modulus than the mean value.
Figure 4.5. Manually generated microstructures containing ~ 90% circular particles by volume.

Table 4.1. Effective moduli of the six model PBX 9501 microstructures from FEM calculations six-noded triangular elements. $E$ is the Young’s modulus and $\nu$ is the Poisson’s ratio.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Model RVE</th>
<th>Mean</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$E$ (MPa)</td>
<td>1013</td>
<td>116</td>
<td>126</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.35</td>
<td>0.34</td>
<td>0.32</td>
</tr>
</tbody>
</table>
The effective Poisson’s ratios of the six RVEs range from 0.25 to 0.34, with a mean of 0.33. The mean Poisson’s ratio of the RVEs is not much different from the measured value for PBX 9501. For models 1, 2, and 3, the effective Poisson’s ratio is within 10% of that of PBX 9501. However, the Poisson’s ratio of model 4 is 25% higher and those of models 5 and 6 are 20% and 28% lower than the Poisson’s ratio of PBX 9501, respectively. The two-dimensional Poisson’s ratios of models 4, 5, and 6 are 0.79, 0.39, and 0.33, respectively. In comparison, the two-dimensional Poisson’s ratio of PBX 9501 is 0.54. Since, these two-dimensional values reflect the actual strains obtained from the two-dimensional finite element calculations, it is clear that model 4 is too compliant while models 5 and 6 are too stiff, compared to PBX 9501. These observations are in agreement with those made regarding Young’s modulus in the previous paragraph and are attributable to the amount of binder along the edge of a RVE.

On average, the FEM estimate of Young’s modulus is around 13% of the experimentally determined value for PBX 9501. The reason for this difference could be that preferential stress paths (stress-bridging) in real microstructures lead to increased stiffness. Results shown in Figure 4.4 indicate that the difference between estimates from two- and three-dimensional models is not large. Hence, it is unlikely that the lower stiffness of the six model RVEs is due to the use of two-dimensional models.

It is possible that the Young’s modulus is underestimated by the six RVEs because the volume fraction of particles in each of these microstructures is lower than 92%. Figure 4.6(a) shows a model containing 92% particles by volume that is a modified version of model 6 in Figure 4.5. The effective Young’s modulus of the RVE containing 92% particles is 218 MPa and the effective Poisson’s ratio is 0.28. In comparison, model 6 contains around 90% particles by volume and has an estimated Young’s modulus of 192 MPa and a Poisson’s ratio of 0.25. Though there is some increase in the Young’s modulus due to increase in particle volume fraction, the value is still around 20% that of PBX 9501. Hence, the volume fraction cannot be the only factor leading to underestimation of the Young’s modulus by the manually generated microstructures.

If a 256×256 square grid is overlaid on top of the model shown in Figure 4.6(a) and cells in the grid are assigned HMX properties if they contain more than 50% particle
and binder properties otherwise (referred to as the "square grid overlay method"), the new microstructure shown in Figure 4.6(d) is obtained. The RVE in Figure 4.6(d) was modeled using $256 \times 256$ four-noded square finite elements. The modified model predicts a Young’s modulus of 800 MPa and a Poisson’s ratio of 0.14. The modulus is now closer to that of PBX 9501 but the Poisson’s ratio is much lower.

The stiffer response for the model shown in Figure 4.6(d) is partially due to increased stiffness of four-noded finite elements. To eliminate the possibility that the stiffer response of the modified model is due to element locking caused by the nearly incompressible binder, the binder was also modeled as a two-parameter Mooney-Rivlin rubber

![Figure 4.6](image.png)

**Figure 4.6.** Microstructure containing 92% particles modeled with six-noded triangles and four-noded squares.
instead of a linear elastic material. An incremental analysis using the Mooney-Rivlin material model yielded values of Young’s modulus and Poisson’s ratio that were within 5% of those for the linear elastic models. This result implies that the difference between the effective properties of the RVEs in Figures 4.6(c) and 4.6(d) is primarily due to the slight difference in microstructure. The same behavior has also been observed for all the models shown in Figure 4.5.

The model in Figure 4.6(d) has a Young’s modulus that is four times higher than that of the model in Figure 4.6(c). This result suggests that the square grid overlay method can lead to the automatic incorporation of preferential stress paths into RVEs containing high volume fractions of particles. In addition, it is easier to generate a square mesh and use the square grid overlay method than to model circular particles using triangular elements. Hence, the square grid overlay method is used to model microstructures based on the actual particle size distribution of PBX 9501.

4.5.2 Randomly generated microstructures

A micrograph of PBX 9501 [18] is shown in Figure 4.7. The HMX particles are shown to be irregularly shaped and present in a large number of sizes. Two length scales can be identified from the micrograph. The first is the scale of the larger particles that occupy most of the volume. The second scale is that of the particles filling the interstitial spaces between the larger particles. Because of these two different length scales, it is extremely difficult to use a digital image at a single scale to generate two-dimensional microstructures of PBX 9501. The approach taken in this work is to simplify the shape of the particles and automatically generate particle distributions that approximate the actual microstructure.

The preferred method for generating close packed microstructures from a set of particles is to use Monte Carlo based molecular dynamics techniques [92] or Newtonian motion based techniques [93]. In both methods, a distribution of particles is allocated to the grid points of a rectangular lattice using a random placement method. Molecular dynamics simulations or Newtonian dynamics calculations are then carried out on the system of particles to reach the packing fraction that corresponds to equilibrium. A weighted Voronoi tessellation [94] is then carried out on the particles with the weights
determined by the sizes of the particles. The particles are next moved towards the center of the packing volume while maintaining that they remain inside their respective Voronoi cells. The process is repeated until all the particles are as tightly packed as possible. Periodicity of the particles at the boundaries is maintained by specifying extra particles at the boundaries that move in and out of the volume. This process, with some modifications, has been the only efficient method of generating close packed systems of particles in three dimensions. However, it is difficult to get packing fractions of more than 70-75% when using spherical particles. It is also quite time consuming to generate a tight packing.

In two dimensions, a faster method can be used for generating particle distributions, that is random sequential packing. The largest particles are placed randomly in the volume followed by progressively smaller particles. If there is any overlap between a new particle and the existing set, the new particle is moved to a new position. If a particle cannot be placed in the volume after a certain number of iterations, the next lower sized particle is chosen and the process is continued until the required volume fraction is achieved. Though this method does not preserve the particle size distributions as accurately as the Monte Carlo based molecular dynamics methods, it is much faster and can be used to generate high packing fractions in two dimensions without particle
locking. In three dimensions, this method is highly inefficient and packing above 60% is extremely time consuming to achieve.

4.5.2.1 Circular particles - PBX 9501 dry blend

HMX particle size distributions of the dry blend of PBX 9501 have been listed by Wetzel [8] and Rae et al. [95]. The coarse and fine particles are blended in a ratio of 1:3 by weight and compacted to form PBX 9501. Four microstructures based on the particle size distribution of the dry blend are shown in Figure 4.8. The number of particles used for the four microstructures are 100, 200, 300, and 400. The RVE widths are 0.65 mm, 0.94 mm, 1.13 mm and 1.325 mm, respectively. The particles occupy a volume fraction of about 85-86%. The remaining volume is assumed to be occupied by a mixture of binder and fine particles of HMX that are well separated in size from the smallest particles shown in the RVEs. This ‘dirty’ binder contains around 36% particles by volume.

Particles in the RVEs were assigned HMX properties and the elastic properties of the dirty binder were calculated using the differential effective medium approximation [28]. The Young’s modulus of the dirty binder used in the calculations was 2.0816 MPa and the Poisson’s ratio was 0.4813. Two sizes of square grids were used for overlaying on the RVEs: 256×256 and 350×350. The square grid overlay method was applied to assign materials to grid cells. Each cell in the grid was modeled using a four-noded finite element. Table 4.2 shows the effective Young’s modulus and Poisson’s ratio predicted for the four models of the dry blend of PBX 9501.

The FEM calculations overestimate the effective Young’s moduli of PBX 9501 by 200% to 400% if the 256×256 grid is used. If the 350×350 grid is used the effective Young’s moduli vary from 100% to 300% of that of PBX 9501. The effective Poisson’s ratio is underestimated considerably in both cases. The stiffer response of these RVEs is partly due to the creation of continuous stress paths across a RVE when a regular grid is overlaid on the RVE and partly because four-noded elements are inherently stiffer [87]. It can also be seen that the effective Young’s modulus increases as the number of particles in the RVE increases. This is because the same grid has been used for the four microstructures, leading to poorer resolution of the geometry with increasing particle density per grid cell.
Figure 4.8. Models based on the dry blend of PBX 9501 containing circular particles.

Table 4.2. Effective elastic moduli of the four models of the dry blend of PBX 9501.

<table>
<thead>
<tr>
<th>No. of Particles</th>
<th>Size (mm)</th>
<th>Young’s Modulus (MPa)</th>
<th>Poisson’s Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FEM 256×256 350×350</td>
<td>Expt. 256×256 350×350</td>
</tr>
<tr>
<td>100</td>
<td>0.65</td>
<td>1959 968</td>
<td>0.22 0.20 0.35</td>
</tr>
<tr>
<td>200</td>
<td>0.94</td>
<td>2316 1488</td>
<td>0.23 0.23 0.35</td>
</tr>
<tr>
<td>300</td>
<td>1.13</td>
<td>2899 2004</td>
<td>0.25 0.24 0.35</td>
</tr>
<tr>
<td>400</td>
<td>1.33</td>
<td>4350 2845</td>
<td>0.25 0.25 0.35</td>
</tr>
</tbody>
</table>
4.5.2.2 Circular particles - pressed PBX 9501

Figure 4.9 shows four RVEs based on the particle size distribution of pressed PBX 9501 [18]. The pressing process leads to particle breakage and hence the larger volume fraction of smaller sized particles. Fewer larger sized particles remain as is reflected in the generated microstructures containing 100, 200, 500, and 1000 particles. In this case, the RVE widths are 0.36 mm, 0.42 mm, 0.535 mm, and 0.68 mm, respectively. Thus, the 1000 particle RVE for the pressed piece has dimensions similar to the 100 particle RVE for the dry blend. The size of the RVE that can be adequately discretized is therefore smaller for the pressed piece. Each RVE was discretized into both 256×256 and 350×350 four-noded elements. Each element was assigned material properties according to the square grid overlay method.

The particles in the RVEs occupy volume fractions from 0.86 to 0.89 and the target volume fraction of 0.92 is not attained in any of the RVEs. A dirty binder, whose properties were calculated using the differential effective medium approach, was used in the effective stiffness calculations. The effective moduli of the dirty binder for the four models are shown in Table 4.3. The effective Young’s modulus and Poisson’s ratio of the four RVEs from FEM calculations are shown in Table 4.4. The 256×256 element models overestimate the Young’s modulus of PBX 9501 by factors increasing from 3 to 6 with increasing RVE size. The estimates from the 350×350 element models are lower but still 2 to 5 times higher than the Young’s modulus of PBX 9501. The estimated Poisson’s ratios are quite low compared to that of PBX 9501.

The four models based on pressed PBX 9501 predict Young’s moduli that are 1.5 to 2 times higher than values predicted by models based on the dry blend of PBX 9501. For the 100 and 200 particle pressed PBX 9501 models, the single large particle contributes considerably to the stiffer response. For the 500 and 1000 particle pressed PBX 9501 models, errors in the discretization of particle boundaries lead to additional stress bridging paths and hence a stiffer response is obtained.
Figure 4.9. Models based on the particle size distribution of pressed PBX 9501 containing circular particles.

Table 4.3. Material properties of the dirty binder for the four pressed piece based PBX 9501 microstructures. \( f_p \) is the volume fraction of particles.

<table>
<thead>
<tr>
<th>No. of Particles</th>
<th>( f_p ) in binder</th>
<th>Properties of dirty binder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( f_p )</td>
<td>E (MPa)</td>
</tr>
<tr>
<td>100</td>
<td>0.89</td>
<td>1.583</td>
</tr>
<tr>
<td>200</td>
<td>0.87</td>
<td>2.1395</td>
</tr>
<tr>
<td>500</td>
<td>0.86</td>
<td>2.713</td>
</tr>
<tr>
<td>1000</td>
<td>0.855</td>
<td>2.952</td>
</tr>
</tbody>
</table>

Table 4.4. Effective elastic moduli of the four models of pressed PBX 9501.

<table>
<thead>
<tr>
<th>No. of Particles</th>
<th>Size (mm)</th>
<th>Young’s Modulus (MPa)</th>
<th>Poisson’s Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FEM 256\times256</td>
<td>Expt. 350\times350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FEM 256\times256</td>
<td>Expt. 350\times350</td>
</tr>
<tr>
<td>100</td>
<td>0.36</td>
<td>2925</td>
<td>1798</td>
</tr>
<tr>
<td>200</td>
<td>0.42</td>
<td>3342</td>
<td>2408</td>
</tr>
<tr>
<td>500</td>
<td>0.54</td>
<td>5256</td>
<td>3994</td>
</tr>
<tr>
<td>1000</td>
<td>0.68</td>
<td>6171</td>
<td>4756</td>
</tr>
</tbody>
</table>
4.5.2.3 Square particles - pressed PBX 9501

With an increase in particle volume fraction, there is an increase in the number of particle-particle contacts in particulate composites. If the particles in a RVE of such a material are circular, triangular elements cannot be used to discretize the RVE because of poor element shapes in regions of contact. Additionally, a rectangular grid cannot represent the geometry of circular particles accurately. An alternative is to use square particles that are aligned with a rectangular grid to represent the microstructure.

The particles shown in the three microstructures in Figure 4.10 are based on the size distribution of pressed PBX 9501. These distributions have been generated by placing square particles in a random sequential manner in a square grid. The smallest particles occupy a single subcell of the grid. Larger particles are chosen from the particle size distribution so that they fit into an integer multiple of the grid size.

In the three models shown in Figure 4.10, the particle size distribution for the pressed piece is truncated so that the smallest (≤ 30 microns) particle sizes in the distribution are not used in order that the grid size does not become too large. The RVEs are filled with particles to volume fractions of about 86-87%. The remaining volume is assumed to be occupied by a dirty binder. The number of particles in the first model is 700 and the RVE width is around 3.6 mm. The second model contains 2,800 particles and the RVE width is about 5.3 mm, while the third model contains 11,600 particles and has a width of 9 mm. Note that these RVEs are considerably larger than those used for the circular particles. Smaller RVEs are not used because of the difficulties associated with fitting particles into integer multiples of subcell widths. The properties of the dirty binder for the three models are shown in Table 4.5.

Finite element calculations were performed on the three models using regular grids of 256×256 square elements. Table 4.6 shows the effective Young’s modulus and Poisson’s ratio obtained from the three RVEs. The FEM estimates of Young’s modulus are 9 times higher than the Young’s modulus of PBX 9501. The higher stiffness obtained from the FEM calculations is partly because the large number of contacts between particles lead essentially to a continuous particle phase containing pockets of binder.
Figure 4.10. Models with square particles based on the size distribution of pressed PBX 9501.

<table>
<thead>
<tr>
<th>No. of Particles</th>
<th>Size of Particles</th>
<th>Properties of Dirty Binder</th>
<th>E (MPa)</th>
<th>ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>3.6×3.6 mm²</td>
<td>0.868 in binder</td>
<td>2.358</td>
<td>0.4799</td>
</tr>
<tr>
<td>2800</td>
<td>5.3×5.3 mm²</td>
<td>0.866 in binder</td>
<td>2.448</td>
<td>0.4795</td>
</tr>
<tr>
<td>11600</td>
<td>9.0×9.0 mm²</td>
<td>0.863 in binder</td>
<td>2.588</td>
<td>0.4788</td>
</tr>
</tbody>
</table>

Table 4.5. Material properties of the dirty binder for the three PBX microstructures with square particles.

Table 4.6. Effective stiffnesses of the model microstructures with square particles.

<table>
<thead>
<tr>
<th>No. of Particles</th>
<th>Size (mm)</th>
<th>Young’s Modulus (MPa)</th>
<th>Poisson’s Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FEM (256×256)</td>
<td>Expt.</td>
<td>FEM (256×256)</td>
</tr>
<tr>
<td>700</td>
<td>3.6</td>
<td>9119</td>
<td>1013</td>
</tr>
<tr>
<td>2800</td>
<td>5.3</td>
<td>9071</td>
<td>1013</td>
</tr>
<tr>
<td>11600</td>
<td>9.0</td>
<td>9593</td>
<td>1013</td>
</tr>
</tbody>
</table>
Micrographs of PBX 9501 show that there is considerable damage in the particles, binder and the particle-binder interface [95]. Better estimates of the effective properties can probably be obtained by incorporating damage in the models of PBX 9501 discussed above. However, this issue is not explored in this work because the amount and type of damage is difficult to quantify in polymer bonded explosives.

### 4.6 Effective moduli of PBX 9501

Of the various microstructures of PBX 9501 explored in the previous section, the best estimate of the Young’s modulus of PBX 9501 is provided by the 100 particle model of the dry blend of PBX 9501 shown in Figure 4.8, overlaid by a $\times$350 grid. The effective properties of PBX 9501 shown in this section have been calculated at different temperatures and strain rates using the 100 particle model of Figure 4.8. Instead of the experimentally determined values of moduli of HMX, data from molecular dynamics (MD) simulations [15] have been used. The Young’s modulus of HMX from MD simulations is 17,700 MPa and the Poisson’s ratio is 0.21 compared to a Young’s modulus of 15,300 MPa and a Poisson’s ratio of 0.32 from experimental data. The Young’s modulus of HMX is assumed constant at the temperatures and strain rates considered.

The PBX 9501 binder data collected from various sources [4, 5, 8, 19] are listed in Table 4.7. The data are sorted in order of decreasing temperature followed by increasing strain rate. As shown in Table 4.7, the Young’s modulus of the binder generally increases with increase in strain rate and with decrease in temperature though some of the available data do not follow this trend. Since values for the Poisson’s ratio of the binder are not available, a value of 0.49 has been used for all cases. However, the value is likely to be lower near the glass transition temperature of estane (around -33°C). As before, a dirty binder has been used for the grid cells not fully occupied by particles. The differential effective medium approximation [28] has been used to calculate the effective properties of the dirty binder using the moduli of HMX and the binder. Table 4.7 also shows the dirty binder properties used in the simulations. It is interesting to note that the Poisson’s ratio of the dirty binder does not change significantly even though the Young’s modulus
Table 4.7. Material properties used to calculate the effective moduli of PBX 9501 for different temperatures and strain rates. Numbers in square brackets refer to the source of the binder data.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Strain Rate (/s)</th>
<th>HMX Young’s Modulus (MPa)</th>
<th>HMX Poisson’s Ratio</th>
<th>PBX 9501 Binder Young’s Modulus (MPa)</th>
<th>PBX 9501 Binder Poisson’s Ratio</th>
<th>’Dirty’ Binder Young’s Modulus (MPa)</th>
<th>’Dirty’ Binder Poisson’s Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.005</td>
<td>17700</td>
<td>0.21</td>
<td>0.59 [8]</td>
<td>0.49</td>
<td>2.15</td>
<td>0.479</td>
</tr>
<tr>
<td>25</td>
<td>0.008</td>
<td>17700</td>
<td>0.21</td>
<td>0.73 [8]</td>
<td>0.49</td>
<td>2.66</td>
<td>0.479</td>
</tr>
<tr>
<td>25</td>
<td>0.034</td>
<td>17700</td>
<td>0.21</td>
<td>0.81 [8]</td>
<td>0.49</td>
<td>2.95</td>
<td>0.479</td>
</tr>
<tr>
<td>25</td>
<td>0.049</td>
<td>17700</td>
<td>0.21</td>
<td>0.82 [8]</td>
<td>0.49</td>
<td>2.99</td>
<td>0.479</td>
</tr>
<tr>
<td>25</td>
<td>2400</td>
<td>17700</td>
<td>0.21</td>
<td>300 [5]</td>
<td>0.49</td>
<td>1001</td>
<td>0.474</td>
</tr>
<tr>
<td>22</td>
<td>0.001</td>
<td>17700</td>
<td>0.21</td>
<td>0.47 [19]</td>
<td>0.49</td>
<td>1.71</td>
<td>0.479</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>17700</td>
<td>0.21</td>
<td>1.4 [19]</td>
<td>0.49</td>
<td>5.10</td>
<td>0.479</td>
</tr>
<tr>
<td>22</td>
<td>2200</td>
<td>17700</td>
<td>0.21</td>
<td>3.3 [19]</td>
<td>0.49</td>
<td>12.0</td>
<td>0.479</td>
</tr>
<tr>
<td>16</td>
<td>1700</td>
<td>17700</td>
<td>0.21</td>
<td>22.5 [4]</td>
<td>0.49</td>
<td>81.5</td>
<td>0.479</td>
</tr>
<tr>
<td>0</td>
<td>0.001</td>
<td>17700</td>
<td>0.21</td>
<td>0.85 [19]</td>
<td>0.49</td>
<td>3.10</td>
<td>0.479</td>
</tr>
<tr>
<td>0</td>
<td>1700</td>
<td>17700</td>
<td>0.21</td>
<td>246 [4]</td>
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<td>833</td>
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</tr>
<tr>
<td>0</td>
<td>2200</td>
<td>17700</td>
<td>0.21</td>
<td>4 [19]</td>
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<td>14.6</td>
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</tr>
<tr>
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<td>0.001</td>
<td>17700</td>
<td>0.21</td>
<td>1.4 [19]</td>
<td>0.49</td>
<td>5.10</td>
<td>0.479</td>
</tr>
<tr>
<td>-15</td>
<td>1</td>
<td>17700</td>
<td>0.21</td>
<td>5.7 [19]</td>
<td>0.49</td>
<td>20.7</td>
<td>0.479</td>
</tr>
<tr>
<td>-15</td>
<td>1000</td>
<td>17700</td>
<td>0.21</td>
<td>1600 [19]</td>
<td>0.49</td>
<td>4082</td>
<td>0.458</td>
</tr>
<tr>
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<td>17700</td>
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<td>1.6 [19]</td>
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<td>5.83</td>
<td>0.479</td>
</tr>
<tr>
<td>-20</td>
<td>1200</td>
<td>17700</td>
<td>0.21</td>
<td>1600 [19]</td>
<td>0.49</td>
<td>4082</td>
<td>0.458</td>
</tr>
<tr>
<td>-20</td>
<td>1700</td>
<td>17700</td>
<td>0.21</td>
<td>1333 [4]</td>
<td>0.49</td>
<td>3556</td>
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</tr>
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<td>17700</td>
<td>0.21</td>
<td>5.7 [19]</td>
<td>0.49</td>
<td>20.7</td>
<td>0.479</td>
</tr>
<tr>
<td>-40</td>
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<td>17700</td>
<td>0.21</td>
<td>5.3 [4]</td>
<td>0.49</td>
<td>19.3</td>
<td>0.479</td>
</tr>
<tr>
<td>-40</td>
<td>1300</td>
<td>17700</td>
<td>0.21</td>
<td>1000 [19]</td>
<td>0.49</td>
<td>2838</td>
<td>0.464</td>
</tr>
</tbody>
</table>
can vary considerably depending on the modulus of the PBX 9501 binder.

Table 4.8 shows the effective properties of the model RVE computed using finite elements along with the available experimental data on PBX 9501. The experimental data are within 15% of the finite element estimates for temperatures close to 25°C and at low strain rates. Good agreement is also observed for the data near 16°C and at high strain rates. However, at 0°C and a strain rate of 2200/s the experimental value is around 2 times the predicted values of Young’s modulus while at -20°C and high strain rate, the experimental value is half the estimate. Experimental data on the Poisson’s ratio of PBX 9501 are available only at 25°C and 0.005/s strain rate. The predicted Poisson’s ratio under these conditions is considerably lower that the experimental value. Since the Poisson’s ratio is highly sensitive to numerical error [96], more accurate numerical calculations may be required to resolve this issue.

These results show that, based on existing data on PBX 9501, it is not possible to conclude that the effective moduli of PBX 9501 can be predicted accurately if the moduli of its constituents are known for various temperatures and strain rates. However, the results do show that for certain RVEs, close approximations to the effective Young’s modulus of PBX 9501 can be obtained from two-dimensional finite element simulations.

4.7 Summary and conclusions

A two-dimensional finite element based method for approximating the effective elastic moduli of particulate composites has been presented. This approach has been applied to representative volume elements (RVEs) containing circular particles for volume fractions from 0.1 to 0.92. The estimated Young’s moduli and Poisson’s ratios have been found to closely approximate those from differential effective medium approximations. Comparisons with three-dimensional finite element simulations have also shown that the two-dimensional approach provides good approximations for RVEs containing polydisperse spherical particles. The estimates of Young’s modulus from three-dimensional models have been found to be slightly higher than from two-dimensional models. On the other hand, the Poisson’s ratios from three-dimensional models have been found to be lower than estimates from two-dimensional models.
Table 4.8. Effective Young’s modulus from finite element simulations of a 100 particle model of the dry blend of PBX 9501. Numbers in square brackets refer to the source of the PBX 9501 data.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Strain Rate (/s)</th>
<th>FEM Estimates</th>
<th>Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Young’s Modulus (MPa)</td>
<td>Poisson’s Ratio</td>
</tr>
<tr>
<td>25</td>
<td>0.005</td>
<td>1001</td>
<td>0.19</td>
</tr>
<tr>
<td>25</td>
<td>0.01</td>
<td>1080</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.034</td>
<td>1123</td>
<td>0.20</td>
</tr>
<tr>
<td>25</td>
<td>0.05</td>
<td>1129</td>
<td>0.20</td>
</tr>
<tr>
<td>25</td>
<td>2400</td>
<td>11273</td>
<td>0.31</td>
</tr>
<tr>
<td>22</td>
<td>0.001</td>
<td>926</td>
<td>0.17</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>1399</td>
<td>0.23</td>
</tr>
<tr>
<td>22</td>
<td>2200</td>
<td>2050</td>
<td>0.26</td>
</tr>
<tr>
<td>16</td>
<td>1700</td>
<td>4981</td>
<td>0.30</td>
</tr>
<tr>
<td>0</td>
<td>0.001</td>
<td>1144</td>
<td>0.21</td>
</tr>
<tr>
<td>0</td>
<td>1700</td>
<td>10808</td>
<td>0.31</td>
</tr>
<tr>
<td>0</td>
<td>2200</td>
<td>2243</td>
<td>0.27</td>
</tr>
<tr>
<td>-15</td>
<td>0.001</td>
<td>1399</td>
<td>0.23</td>
</tr>
<tr>
<td>-15</td>
<td>1</td>
<td>2652</td>
<td>0.28</td>
</tr>
<tr>
<td>-15</td>
<td>1000</td>
<td>14602</td>
<td>0.28</td>
</tr>
<tr>
<td>-20</td>
<td>0.001</td>
<td>1481</td>
<td>0.23</td>
</tr>
<tr>
<td>-20</td>
<td>1200</td>
<td>14602</td>
<td>0.28</td>
</tr>
<tr>
<td>-20</td>
<td>1700</td>
<td>14291</td>
<td>0.29</td>
</tr>
<tr>
<td>-40</td>
<td>0.001</td>
<td>2652</td>
<td>0.28</td>
</tr>
<tr>
<td>-40</td>
<td>0.001</td>
<td>2562</td>
<td>0.27</td>
</tr>
<tr>
<td>-40</td>
<td>1300</td>
<td>13778</td>
<td>0.29</td>
</tr>
</tbody>
</table>

a - experimental data are for a strain rate of 0.001/s.
b - experimental data are for a strain rate of 0.011/s and a temperature of 27°C.
c - experimental data are for a strain rate of 2250/s and a temperature of 17°C.
d - experimental data are for a strain rate of 2250/s.
Since polymer bonded explosives such as PBX 9501 contain two widely separated particle sizes, a number of manually generated microstructures of PBX 9501 have been simulated. The models were designed to contain a few large particles and a larger number of smaller interstitial particles while avoiding particle-particle contact. Such models have been found to underestimate the Young’s modulus of PBX 9501 considerably when discretized with triangular elements. However, when the same models are discretized with square elements, considerably different estimates of Young’s modulus are obtained depending on the degree of discretization. Hence, it is extremely difficult to determine an appropriate RVE for high modulus contrast and high volume fraction particulate composites that has the optimal size, number of particles, particle shapes and size distributions. The RVE also has to be such that it can be easily discretized using elements that are accurate and relatively computationally inexpensive.

Randomly generated microstructures based on the particle size distribution of PBX 9501 show that the size of the RVE plays a lesser role in the determination of the effective Young’s modulus than the amount of discretization used, even for highly refined meshes. If aligned square particles are used instead of circular particles, the predicted moduli are considerably higher than the experimental moduli because contacts between particles increase dramatically. It is also observed that the numerical simulations consistently underestimate the effective Poisson’s ratio. Since the Poisson’s ratio is highly sensitive to numerical error, accurate numerical simulations have to be performed to resolve this issue.

Simulations of PBX 9501 for various temperatures and strain rates suggest that if a RVE is chosen that predicts a reasonable value of Young’s modulus at a given temperature and strain rate, it can be used to obtain acceptable estimates at other temperatures and strain rates. Further experimental data are required to confirm this finding.
CHAPTER 5
APPLICATION OF THE GENERALIZED METHOD OF CELLS TO POLYMER BONDED EXPLOSIVES

5.1 Abstract
The prediction of the effective elastic properties of polymer bonded explosives using direct numerical simulations is computationally expensive because of the high volume fraction of particles in these particulate composites (\(~0.90\)) and the strong modulus contrast between the particles and the binder (\(~20,000\)). The generalized method of cells (GMC) is an alternative to direct numerical simulations for the determination of effective elastic properties of composites. GMC has been shown to be more computationally efficient than finite element analysis based approaches for a range of composites. In this investigation, the applicability of GMC to the determination of effective elastic properties of polymer bonded explosives is explored. GMC is shown to generate excellent estimates of effective moduli for composites containing square arrays of disks at volume fractions less than 0.60 and a modulus contrast of approximately 100. However, for high volume fraction and strong modulus contrast polymer bonded explosives such as PBX 9501, the elastic properties predicted by GMC are found to be considerably lower than finite element based estimates and experimental data. Simulations of model microstructures are performed to show that normal stiffnesses are underestimated by GMC when stress-bridging due to contact between particles is dominant. Additionally, the computational efficiency of GMC decreases rapidly with an increase in the number of subcells used to discretize a representative volume element. The results presented in this work suggest that GMC may not be suitable for calculating the effective elastic properties of high volume fraction and strong modulus contrast particulate composites.
5.2 Introduction

The generalized method of cells (GMC) [76, 75] is a semianalytical method of determining the effective properties of composites. In this method, a representative volume element (RVE) of the composite under consideration is discretized into a regular grid of subcells. Equilibrium and compatibility are satisfied on an average basis across subcells using integrals over subcell boundaries. GMC generates a matrix of algebraic expressions containing information about subcell material properties. The effective stiffness of the composite can be obtained by inverting this matrix.

One advantage of GMC over other numerical techniques is that the full set of effective elastic properties of a composite can be calculated in one step instead of solving a number of boundary value problems with different boundary conditions. GMC has also been found to be more computationally efficient than finite element calculations for fiber reinforced composites [76, 97], since far fewer GMC subcells than finite elements are necessary to obtain the same degree of accuracy. The problem of discretization is also minimized since a regular rectangular grid is used in GMC.

The generalized method of cells is discussed briefly in this work. Effective stiffnesses predicted by this method are compared with accurate numerical predictions for square arrays of disks [73]. The method is then applied to two-dimensional models of a general polymer bonded explosive and to the microstructure of PBX 9501 using a two-step procedure similar to that of Low et al. [98]. GMC estimates of elastic properties are compared with predictions from detailed finite element calculations. The performance of GMC is explored for several microstructures with contacting particles and some shortcomings of the method are identified.

5.3 The generalized method of cells

Figure 5.1 shows a schematic of the RVE, the subcells and the notation [43] used in GMC. In the figure, \((X_1, X_2, X_3)\) is the global coordinate system of the RVE and \((x^{(\alpha)}_1, x^{(\beta)}_2, x^{(\gamma)}_3)\) is the coordinate system local to a subcell denoted by \((\alpha\beta\gamma)\). It is assumed that the displacement function \(u_i^{(\alpha\beta\gamma)}\) varies linearly within a subcell \((\alpha\beta\gamma)\).
Figure 5.1. RVE, subcells and notation used in GMC.
The displacement in a subcell can therefore be expressed as

\[ u_i^{(\alpha \beta \gamma)} (x_1^{(\alpha)}, x_2^{(\beta)}, x_3^{(\gamma)}) = u_i^{(\alpha \beta \gamma)} (X_1, X_2, X_3) + \Phi_i^{(\alpha \beta \gamma)} x_1^{(\alpha)} + \Theta_i^{(\alpha \beta \gamma)} x_2^{(\beta)} + \Psi_i^{(\alpha \beta \gamma)} x_3^{(\gamma)} \]

(5.1)

where \( i \) represents the coordinate direction and takes the values 1, 2 or 3; \( u_i^{(\alpha \beta \gamma)} \) is the mean displacement at the center of the subcell \((\alpha \beta \gamma)\); and \( \Phi_i^{(\alpha \beta \gamma)} \), \( \Theta_i^{(\alpha \beta \gamma)} \), and \( \Psi_i^{(\alpha \beta \gamma)} \) are constants local to the subcell that represent gradients of displacement across the subcell.

The strain-displacement relations for the subcell are given by

\[ \epsilon_{ij}^{(\alpha \beta \gamma)} = \frac{1}{2} (\partial_i u_j^{(\alpha \beta \gamma)} + \partial_j u_i^{(\alpha \beta \gamma)}) \]

(5.2)

where \( \partial_1 = \partial / \partial x_1^{(\alpha)} \), \( \partial_2 = \partial / \partial x_2^{(\beta)} \), and \( \partial_3 = \partial / \partial x_3^{(\gamma)} \). Since polymer bonded explosives are isotropic particulate composites, the following brief description of GMC assumes that the RVE is cubic and all subcells are of equal size. If each subcell \((\alpha \beta \gamma)\) has the same dimensions \((2h, 2h, 2h)\) then the average strain in the subcell is defined as a volume average of the strain field over the subcell as

\[ \left\langle \epsilon_{ij}^{(\alpha \beta \gamma)} \right\rangle_s = \frac{1}{8h^3} \int_{-h}^{h} \int_{-h}^{h} \int_{-h}^{h} a \ dx_1^{(\alpha)} dx_2^{(\beta)} dx_3^{(\gamma)} \epsilon_{ij}^{(\alpha \beta \gamma)} \]

(5.3)

The average strain in the subcell can be obtained in terms of the displacement field variables. It is assumed that there is continuity of traction at the interface of two subcells. The displacements and tractions are assumed to be periodic at the boundaries the RVE. Applying the displacement continuity equations on an average basis over the interfaces between subcells, the average strain in the RVE can be expressed in terms of the subcell strains. The average subcell stresses can be obtained from the subcell strains using the traction continuity condition and the stress-strain relations of the materials in the subcells. A relationship between the subcell stresses and the average strains in the RVE is thus obtained.

For orthotropic, transversely isotropic or isotropic materials, the approach discussed above leads to the decoupling of the normal and shear response of the RVE. This decoupling leads to two systems of equations relating the subcell stresses and the average
strains in the RVE. For the normal components of strain, the system of equations can be written as

\[
\begin{bmatrix}
M_{11} & M_{12} & M_{13} \\
M_{21} & M_{22} & M_{23} \\
M_{31} & M_{32} & M_{33}
\end{bmatrix}
\begin{bmatrix}
T_1 \\
T_2 \\
T_3
\end{bmatrix}
= 2N
\begin{bmatrix}
\mathbf{H} \\
0 \\
0
\end{bmatrix}
\begin{bmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
\epsilon_{33}
\end{bmatrix}
+ 2N
\begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\begin{bmatrix}
\epsilon_{12} \\
\epsilon_{23} \\
\epsilon_{33}
\end{bmatrix}
\begin{bmatrix}
\epsilon_{13} \\
\epsilon_{23} \\
\epsilon_{33}
\end{bmatrix}
\begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\]

(5.4)

where \( N \) is the number of subcells per side of the RVE. The corresponding system of equations for the shear components is of the form

\[
\begin{bmatrix}
M_4 & 0 & 0 \\
0 & M_5 & 0 \\
0 & 0 & M_6
\end{bmatrix}
\begin{bmatrix}
T_{12} \\
T_{23} \\
T_{13}
\end{bmatrix}
= 2N^2
\begin{bmatrix}
\mathbf{H} \\
0 \\
0
\end{bmatrix}
\begin{bmatrix}
\epsilon_{12} \\
\epsilon_{23} \\
\epsilon_{33}
\end{bmatrix}
+ 2N^2
\begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\begin{bmatrix}
\epsilon_{13} \\
\epsilon_{23} \\
\epsilon_{33}
\end{bmatrix}
\begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\]

(5.5)

In equations (5.4) and (5.5) the \( M \) matrices contain material compliance terms. The \( T \) matrices contain the average subcell stresses. The vector \( \mathbf{H} \) contains the dimensions of the subcells. Thus, a sparse system of equations of size \( 3N^2 \) is produced that relates the subcell stresses to the average strains in the RVE. After inverting these equations and with some algebraic manipulation, explicit algebraic expressions for the individual terms of the effective stiffness matrix can be obtained. These stress-strain equations that relate the average RVE stresses to the average RVE strains are of the form

\[
\begin{bmatrix}
\langle \sigma_{11} \rangle \\
\langle \sigma_{22} \rangle \\
\langle \sigma_{33} \rangle \\
\langle \sigma_{12} \rangle \\
\langle \sigma_{31} \rangle \\
\langle \sigma_{23} \rangle
\end{bmatrix}
= \begin{bmatrix}
C_{11}^{\text{eff}} & C_{12}^{\text{eff}} & C_{13}^{\text{eff}} \\
C_{12}^{\text{eff}} & C_{22}^{\text{eff}} & C_{23}^{\text{eff}} \\
C_{13}^{\text{eff}} & C_{23}^{\text{eff}} & C_{33}^{\text{eff}} \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
\langle \epsilon_{11} \rangle \\
\langle \epsilon_{22} \rangle \\
\langle \epsilon_{33} \rangle \\
2 \langle \epsilon_{12} \rangle \\
2 \langle \epsilon_{31} \rangle \\
2 \langle \epsilon_{23} \rangle
\end{bmatrix}
\]

(5.6)

where \( C_{ij}^{\text{eff}} \) are the terms of the effective stiffness matrix. Details of the algebraic expressions for these terms have been published by other researchers [77].

In GMC, the number of equations to be solved is \( O(N^d) \) where \( N \) is the number of subcells and \( d \) is the number of dimensions in the problem. As a result, the computational efficiency of GMC decreases as the number of subcells increases. This issue has been partially resolved [99] by identifying the sparsity characteristics of the system of equations and by using the Harwell-Boeing suite of sparse solvers. The computational efficiency of GMC has been further improved after a reformulation [77, 79] that takes
advantage of the continuity of tractions across subcells to obtain a system of \(O(N^2)\) equations in three dimensions.

Due to decoupling of the normal and shear response of the RVE, the shear components of the stiffness matrix obtained from GMC are the harmonic means of the subcell shear stiffnesses and of the form

\[
\frac{1}{C_{66}^{\text{eff}}} = \frac{1}{N^3} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \sum_{\gamma=1}^{N} \frac{1}{C_{\alpha\beta\gamma}^{(\text{sub})}}.
\]

Bednarcyk and Arnold (2001) suggest that this lack of coupling makes for an “ultra-efficient” micromechanics model. However, this lack of coupling can lead to gross underestimation of shear moduli for high volume fraction and high modulus contrast materials such as polymer bonded explosives. Recently, researchers [82, 83] have attempted to solve the problem by using higher order expansions for the displacement and by explicitly satisfying both subcell equilibrium and compatibility. However, these approaches decrease the computational efficiency of GMC considerably and are not explored in this work.

5.4 Validation - square arrays of disks

In this section, estimates of effective properties from GMC are compared with accurate numerical results for square arrays of disks. Square RVEs containing square arrays of disks exhibit square symmetry. The two-dimensional linear elastic stress-strain relation for these RVEs can be written as

\[
\begin{bmatrix}
\langle \sigma_{11} \rangle_V \\
\langle \sigma_{22} \rangle_V \\
\langle \sigma_{12} \rangle_V
\end{bmatrix} =
\begin{bmatrix}
K_{\text{eff}} + \mu_{\text{eff}}^{(1)} & K_{\text{eff}} - \mu_{\text{eff}}^{(1)} & 0 \\
K_{\text{eff}} - \mu_{\text{eff}}^{(1)} & K_{\text{eff}} + \mu_{\text{eff}}^{(1)} & 0 \\
0 & 0 & \mu_{\text{eff}}^{(2)}
\end{bmatrix}
\begin{bmatrix}
\langle \epsilon_{11} \rangle_V \\
\langle \epsilon_{22} \rangle_V \\
2 \langle \epsilon_{12} \rangle_V
\end{bmatrix}
\]

(5.8)

where \(K_{\text{eff}}\) is the two-dimensional effective bulk modulus, \(\mu_{\text{eff}}^{(1)}\) is the effective shear modulus when a shear stress is applied along the diagonals of the RVE, and \(\mu_{\text{eff}}^{(2)}\) is the effective shear modulus when a shear stress is applied along the edges of the RVE. These three effective moduli have been determined accurately, using an integral equation approach, by Greengard and Helsing (1998) for square arrays of disks containing a range of disk volume fractions.
To compare the effective moduli predicted by GMC with those from the integral equation calculations [73], RVEs containing disk volume fractions from 0.10 to 0.70 were created. These RVEs were discretized into $64 \times 64$ equal sized subcells. The effective stiffness matrix of each RVE was calculated using GMC. Finally, the two-dimensional effective moduli for each RVE were calculated from the effective stiffness matrix using the relations

$$K_{\text{eff}} = 0.5(C_{11}^{\text{eff}} + C_{12}^{\text{eff}}), \quad \mu_{\text{eff}}^{(1)} = 0.5(C_{11}^{\text{eff}} - C_{12}^{\text{eff}}), \quad \mu_{\text{eff}}^{(2)} = C_{66}^{\text{eff}}.$$ (5.9)

Figure 5.2 shows the moduli predicted by GMC and those from the integral equation method of Greengard and Helsing (G&H) for disk volume fractions from 0.10 to 0.70. The material properties of the disks and the binder used in the calculations are shown in Table 5.1. The effective bulk moduli ($K_{\text{eff}}$) and diagonal shear moduli ($\mu_{\text{eff}}^{(1)}$) obtained from the GMC calculations are within 4% of those obtained by the integral equation method for all volume fractions up to 0.60. At a volume fraction of 0.70, the GMC predictions for bulk modulus and diagonal shear modulus are 4% and 11% less, respectively. For the shear modulus $\mu_{\text{eff}}^{(2)}$, the GMC predictions are around 4% to 10% less than the estimates of Greengard and Helsing for volume fractions from 0.10 to 0.60. The difference is around 24% for a volume fraction of 0.70.

These results show that GMC estimates are quite accurate for composites containing square arrays of disks with volume fractions up to 0.60, confirming results reported elsewhere [76]. In the next section, GMC is used to determine the effective properties of models of polymer bonded explosives and the results are compared to detailed finite element calculations and experimental data.

### 5.5 Modeling polymer bonded explosives

Polymer bonded explosive (PBX) materials typically contain around 90% by volume of particles surrounded by a binder. The particles consist of a mixture of coarse and fine grains with the finer grains forming a filler between coarser grains. Modeling the microstructure of these materials is difficult due to the complex shapes of HMX particles and the large range of particle sizes. Two-dimensional approximations of the microstructure of PBXs based on digital images [90] have been used to study some aspects of the
Figure 5.2. Comparison of effective moduli of square arrays of disks from Greengard and Helsing (G&H) [73] and GMC calculations.

Table 5.1. Component properties used by Greengard and Helsing [73].

<table>
<thead>
<tr>
<th></th>
<th>Young’s Modulus (MPa)</th>
<th>Poisson’s Ratio</th>
<th>Two-dimensional Bulk Modulus (MPa)</th>
<th>Shear Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disks</td>
<td>324</td>
<td>0.20</td>
<td>225</td>
<td>135</td>
</tr>
<tr>
<td>Binder</td>
<td>2.7</td>
<td>0.35</td>
<td>3.3</td>
<td>1</td>
</tr>
</tbody>
</table>
micromechanics of PBXs. However, such microstructures are difficult to generate and require complex image processing techniques and excellent image quality to accurately capture details of the material. A combination of Monte Carlo and molecular dynamics techniques has also been used to generate three-dimensional models of PBXs [91]. Microstructures containing spheres and oriented cubes have been generated using these techniques and appear to represent PBX microstructures well. However, the generation of microstructures using dynamics-based methods is extremely time consuming when tight particle packing is required, as is the case for volume fractions above 0.70.

Comparisons of finite element predictions with analytical solution for the effective properties of composites (Chapters 3 and 4) have shown that detailed finite element estimates can be used as a benchmark to check the accuracy of predictions from other numerical techniques. In this investigation, manually generated PBX microstructures containing symmetrically distributed circular particles are used initially to compare GMC and finite element predictions. The two-dimensional microstructures contain 90% particles by volume and use two particle length scales. Two-dimensional models containing randomly distributed circular particles that reflect the actual particle size distribution of PBX 9501 are next modeled with GMC and the results compared to finite element estimates.

The material properties used for the particles, the binder, and PBX9501 in these calculations are shown in Table 5.2. These properties correspond to those of HMX (the explosive particles), the binder, and PBX 9501 at 25°C and a strain rate of 0.05/s [8].

<table>
<thead>
<tr>
<th>Material</th>
<th>$E$ (MPa)</th>
<th>$\nu$</th>
<th>$C_{11} = C_{22}$ (MPa)</th>
<th>$C_{12}$ (MPa)</th>
<th>$C_{66}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles</td>
<td>15300</td>
<td>0.32</td>
<td>21894</td>
<td>10303</td>
<td>5795</td>
</tr>
<tr>
<td>Binder</td>
<td>0.7</td>
<td>0.49</td>
<td>11.97</td>
<td>11.51</td>
<td>0.235</td>
</tr>
<tr>
<td>PBX 9501</td>
<td>1013</td>
<td>0.35</td>
<td>1626</td>
<td>875</td>
<td>375</td>
</tr>
</tbody>
</table>

Table 5.2. Experimentally determined elastic moduli and stiffness of PBX 9501 and its constituents [8].
5.5.1 Simplified models of PBX materials

GMC and finite element calculations were performed for the six, manually generated, simplified model microstructures of polymer bonded explosives shown in Figure 5.3. These representative volume elements (RVEs) contain one or a few relatively large particles surrounded by smaller particles to reflect common particle size distributions of PBXs. The volume fraction of particles in each of these models is around 0.90 ± 0.005. The binder material surrounds all particles in the six microstructures.

For the GMC calculations, a square grid was overlaid on the RVEs to generate subcells. Two different approaches were used to assign materials to subcells before the determination of effective properties of the RVE. In the first approach, referred to as the “binary subcell approach,” a subcell was assigned the material properties of particles if more than 50% of the subcell was occupied by particles. Binder properties were assigned otherwise. Figure 5.4(a) shows a schematic of the binary subcell approach. In the second approach, called the “effective subcell approach,” a method of cells calculation [43] was used to determine the effective properties of a subcell based on the cumulative volume fraction of particles in the subcell [100]. Figure 5.4(b) shows a schematic of the effective subcell approach. After the subcells were assigned material properties, the GMC technique was used to compute the effective properties of the RVE.

Note that the particles are not resolved well when materials are assigned to subcells in this manner if the number of subcells is small. However, the large size of the matrix to be inverted in GMC limits the number of subcells that can be used to discretize the RVE. If the binary subcell approach is used to assign subcell materials, contacting particles are created where there are none in the actual microstructure, leading to the prediction of higher than actual stiffness values. The effective subcell approach improves upon the binary subcell approach by “smearing” the material properties at the boundaries of particles and thus reducing the particle contact artifacts caused by discretization errors.

For validating the GMC results, detailed finite element (FEM) calculations were performed using six-noded triangular elements to accurately model the geometry of the particles. Around 65,000 nodes were used to discretize each of the models. The volume average stress and strain in each RVE was determined for applied normal and shear
Figure 5.3. Manually generated microstructures containing approximately 90% circular particles by volume.

(a) Binary subcell approach.

(b) Effective subcell approach.

Figure 5.4. Schematics of the application of the binary subcell approach and the effective subcell approach in GMC calculations.
displacements. Periodicity was enforced through displacement boundary conditions. Since these finite element calculations serve to validate the GMC calculations, further mesh refinement was explored and the results were found to converge those from the 65,000 node finite element models.

Table 5.3 lists the effective stiffnesses of the six RVEs shown in Figure 5.3 from GMC and FEM calculations. On average, the GMC calculations using the binary subcell approach predict values of $C_{11}^{\text{eff}}$ that are around 2.5 times the FEM based values. The values of $C_{11}^{\text{eff}}$ from the effective subcell approach based GMC calculations are closer to the FEM estimates than the binary subcell based GMC estimates. The GMC and FEM estimates of $C_{12}^{\text{eff}}$ are quite close. The values of $C_{66}^{\text{eff}}$ from GMC are only 10% of the FEM values. The low values of $C_{66}^{\text{eff}}$ are obtained because GMC predict effective shear stiffnesses that are harmonic means of subcell shear stiffnesses. Models 3 and 4 (Figure 5.3) produce agreement in $C_{11}^{\text{eff}}$ and $C_{12}^{\text{eff}}$ between the binary subcell approach based GMC calculations and FEM (within 5%) whereas the other four models produce considerable differences in predictions.

The large differences between the predictions from the binary subcell approach and the effective subcell approach are produced by errors introduced in the discretization process for the binary subcell approach that, in some cases, lead to continuous stress-bridging paths across the RVEs and hence to increased stiffness. However, if the pre-

<table>
<thead>
<tr>
<th>Model</th>
<th>$C_{11}^{\text{eff}}$ (MPa)</th>
<th>$C_{12}^{\text{eff}}$ (MPa)</th>
<th>$C_{66}^{\text{eff}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FEM</td>
<td>GMC</td>
<td>FEM</td>
</tr>
<tr>
<td>1</td>
<td>177</td>
<td>814 479</td>
<td>90 119 103</td>
</tr>
<tr>
<td>2</td>
<td>181</td>
<td>807 477</td>
<td>86 112 103</td>
</tr>
<tr>
<td>3</td>
<td>186</td>
<td>815 193</td>
<td>88 108 89</td>
</tr>
<tr>
<td>4</td>
<td>143</td>
<td>116 142</td>
<td>114 112 124</td>
</tr>
<tr>
<td>5</td>
<td>237</td>
<td>132 323</td>
<td>94 100 104</td>
</tr>
<tr>
<td>6</td>
<td>229</td>
<td>132 334</td>
<td>76 93 100</td>
</tr>
<tr>
<td>Mean</td>
<td>192</td>
<td>471 325</td>
<td>91 107 104</td>
</tr>
</tbody>
</table>
dicted effective stiffnesses shown in Table 5.3 are compared with the experimental effective stiffness of PBX 9501 (shown in Table 5.2), it can be observed that the models predict values of $C_{11}^{\text{eff}}$ and $C_{12}^{\text{eff}}$ that are around 10% of the experimental values. Hence, these simplified models are not appropriate for the modeling of PBX 9501. The next section explores models based on the actual particle size distribution of PBX 9501.

### 5.5.2 Models of PBX 9501

Coarse and fine particles of HMX are blended in a ratio of 1:3 by weight and compacted in the process of manufacturing PBX 9501. Figure 5.5(a) shows four RVEs of PBX 9501 based on the particle size distribution of the dry blend of HMX [8] prior to compaction. Figure 5.5(b) shows four RVEs based on the particle size distribution of pressed PBX 9501 [18]. The larger particles are broken up in the pressing process leading to a larger proportion of smaller particles in pressed PBX 9501. The models of the dry blend have been labeled “DB” while those of pressed PBX 9501 have been labeled “PP”.

GMC calculations were performed on the PBX 9501 RVEs after discretizing each RVE into $100 \times 100$ subcells and assigning materials to subcells using the effective subcell approach. In order to validate the GMC predictions, FEM calculations were also performed on the RVEs after discretizing each RVE into $350 \times 350$ four-noded square elements. The binary subcell approach was applied to assign materials to elements for the FEM calculations.

The particles in each RVE were assigned properties of HMX from Table 5.2. However, since particles occupy 92% of the total volume in actual PBX 9501 while the sample microstructures could be filled only up to $\sim 86\%$, an intermediate homogenization step was required to determine the properties of the binder. To produce the desired 92% volume of particles, a fine-particle filled binder containing 36% particles by volume, or “dirty” binder, was assumed. The effective elastic properties of the dirty binder were calculated using the differential effective medium approximation [28].

Table 5.4 shows the effective stiffness from FEM and GMC calculations for the models of PBX 9501 shown in Figure 5.5. For all microstructures, the values of $C_{11}^{\text{eff}}$ and $C_{22}^{\text{eff}}$ predicted by GMC are less than 5% of the FEM values and less than 10% of the
Figure 5.5. Microstructures containing circular particles based on the particle size distribution of the dry blend (DB) of PBX 9501 and of pressed (PP) PBX 9501.

Table 5.4. Effective stiffness of the model PBX 9501 microstructures from GMC and FEM calculations.
experimental values for PBX 9501 (shown in Table 5.2). The FEM estimates increase with RVE size (varying from 150% to 450% of the experimental values), reflecting the dependence of predicted stiffnesses on microstructure, discretization and particle size distribution. The RVEs contain numerous particle to particle contacts, the number of which increases with increase in RVE size. These contacts lead to significant stress-bridging and hence relatively high values of stiffness as is reflected in the FEM predictions. However, stress-bridging is not incorporated accurately in the GMC approach leading to considerably lower values of effective stiffness. The issue of stress-bridging is further explored in the following section.

The values of $C_{\text{eff}}^{\infty}$ predicted by GMC are around 0.5% of the FEM predictions. This large difference is due to the effective shear stiffness predicted by GMC being the harmonic mean of the subcell shear moduli that provides only a lower bound on the shear stiffness.

## 5.6 Stress-Bridging

Comparisons of effective stiffness properties predicted by GMC with other numerical estimates have shown that GMC performs quite well for low modulus contrast materials with volume fractions below 60%. However, for high modulus contrast materials with high particle volume fractions, GMC usually predicts considerably lower effective stiffnesses than finite element calculations. In this section, GMC is applied to selected microstructures containing stress-bridging and the predicted properties are compared to finite element estimates. The goal is to demonstrate that the effects of stress-bridging on effective properties are inaccurately described by GMC.

### 5.6.1 Corner bridging: X-shaped microstructure

In the RVE shown in Figure 5.6, the particles are square, arranged in the form of an ‘X’, and occupy a volume fraction of 25%. The particles transfer stress through corner contacts. The effective properties of the X-shaped microstructure shown in Figure 5.6 were calculated using the properties of HMX and five different binders with Young’s moduli that range from 0.7 MPa to 7000 MPa, as shown in Table 5.5.
Figure 5.6. RVE used for corner stress-bridging model.

Table 5.5. The elastic properties of the components of the X-shaped microstructure. \( C_{ij} \) are components of the stiffness matrix.

<table>
<thead>
<tr>
<th></th>
<th>Young’s Modulus (MPa)</th>
<th>Poisson’s Ratio</th>
<th>( C_{11} ) (MPa)</th>
<th>( C_{12} ) (MPa)</th>
<th>( 0.5C_{66} ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles</td>
<td>15300</td>
<td>0.32</td>
<td>21894</td>
<td>10303</td>
<td>5795</td>
</tr>
<tr>
<td>Binder a</td>
<td>0.7</td>
<td>0.49</td>
<td>12</td>
<td>11.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Binder b</td>
<td>7</td>
<td>0.49</td>
<td>120</td>
<td>115</td>
<td>2.4</td>
</tr>
<tr>
<td>Binder c</td>
<td>70</td>
<td>0.49</td>
<td>1198</td>
<td>1151</td>
<td>23.5</td>
</tr>
<tr>
<td>Binder d</td>
<td>700</td>
<td>0.49</td>
<td>11980</td>
<td>11510</td>
<td>235</td>
</tr>
<tr>
<td>Binder e</td>
<td>7000</td>
<td>0.49</td>
<td>119799</td>
<td>115101</td>
<td>2349</td>
</tr>
</tbody>
</table>
Figure 5.7 shows the variation in the effective stiffness properties $C_{11}^{\text{eff}}$ and $C_{66}^{\text{eff}}$ of the X-shaped microstructure with increasing Young’s modulus contrast between the particles and the binder ($E_p/E_b$). These effective stiffness properties have been calculated using both finite elements (FEM) (256×256 elements) and GMC (64×64 subcells). The FEM and GMC estimates are in good agreement for Young’s modulus contrasts of 200 or less. For higher Young’s modulus contrasts, the effective stiffness properties predicted by GMC are much lower than those predicted by FEM. Note that the FEM estimates do not change significantly with increased discretization, implying that the solution has converged. The effect of corner singularities is also averaged out while calculating the effective properties using FEM. If it is assumed that the FEM estimates are close to the actual effective moduli of the RVE, the GMC estimates for high modulus contrasts are orders of magnitude lower than the actual effective moduli. Hence, GMC does not capture the stiffening effect of corner contacts accurately.

Since the corner stress-bridging problem involves high stress concentrations that are not resolved well by finite elements, it is possible that the FEM calculations overestimate
the effective properties of the X-shaped microstructure. Such corner singularities are
minimized in the microstructures studied in the next section where the effect of stress-
bridging along particles edges is studied.

5.6.2 Edge bridging

Figure 5.8 shows five RVEs (A through E) in which the degree of stress-bridging
is increased progressively from corner bridging, to partial edge bridging, and finally to
continuous stress-bridging across the RVE. In Figure 5.8, the ‘1’ direction corresponds
to the $x$-axis and the ‘2’ direction corresponds to the $y$-axis.

Model A contains a square particle that occupies 25% of the volume, is centered in
the RVE, and does not have any stress-bridging. Model B contains three particles that
contact along a diagonal of the RVE. In model C, particle contact is increased to produce
a single line of stress-bridging in the $x$-direction along the center of the RVE. Model D
extends the line of contact in the $x$-direction to an area of contact in the $x$-direction. In
Model E, particle bridging across the RVE is extended to both directions. The material
properties of the constituents of PBX 9501 at room temperature and low strain rate were
used for the calculations (Table 5.2). GMC simulations of the RVEs were performed
using $100 \times 100$ subcells while the validating finite element calculations were performed
using approximately 10,000 eight-noded quadrilateral elements. Table 5.6 shows the
effective stiffnesses of the five models obtained from GMC and finite element (FEM)
calculations.

As expected in model A, GMC and FEM predict nearly the same values of effective
stiffness since there is no stress-bridging in the model (the effective stiffness is deter-
mined primarily by the volume fraction occupied by the square particle). However, FEM
calculations for model B show that the diagonal stress-bridge in the model produces a
higher stiffness than would occur if only the volume fraction occupied by the particles
were considered in the calculation of effective stiffness.

The GMC calculations for model B predict values of $C_{11}^{\text{eff}}$ and $C_{12}^{\text{eff}}$ that are lower
than the FEM estimates by a factor of 18. This discrepancy implies that the diagonal
stress-bridge in model B is not detected by the GMC calculations.
Figure 5.8. Progressive stress-bridging models A through E.

Table 5.6. Effective properties of edge bridging models.

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}^{\text{eff}}$ (MPa)</th>
<th>$C_{22}^{\text{eff}}$ (MPa)</th>
<th>$C_{12}^{\text{eff}}$ (MPa)</th>
<th>$0.5C_{66}^{\text{eff}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model A</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Model B</td>
<td>336</td>
<td>19</td>
<td>343</td>
<td>19</td>
</tr>
<tr>
<td>Model C</td>
<td>4095</td>
<td>25</td>
<td>889</td>
<td>24</td>
</tr>
<tr>
<td>Model D</td>
<td>8992</td>
<td>8540</td>
<td>1361</td>
<td>32</td>
</tr>
<tr>
<td>Model E</td>
<td>10017</td>
<td>9042</td>
<td>10052</td>
<td>9042</td>
</tr>
</tbody>
</table>
The FEM estimate of $C_{66}^{\text{eff}}$ for model B is around 1,400 times that from GMC. This difference shows that, in the presence of stress-bridging, the shear stiffness can be considerably underestimated by GMC, even for low volume fraction composites.

Model C has a continuous path through particles along the $x$-axis (the ‘1’ direction) and another continuous particle path along one diagonal. Intuitively, the stress-bridge path along the ‘1’ direction is expected to primarily affect the normal components of stiffness ($C_{11}^{\text{eff}}, C_{12}^{\text{eff}}, C_{22}^{\text{eff}}$) while particle contact along the diagonal is expected to affect the shear stiffness ($C_{66}^{\text{eff}}$). These paths are shown by dashed lines (for normal stress-bridging) and by dotted lines (for shear stress-bridging) in Figure 5.9. Results for model C in Table 5.6 show that FEM predicts a considerable stiffening in the ‘1’ direction while GMC does not appear to account for these stress-bridges. Since the shear stiffness from GMC is simply a harmonic means of the subcell stiffnesses, $C_{66}^{\text{eff}}$ is not affected at all by geometry and only increases in proportion with the volume fraction of particles in the RVE.

The estimates of $C_{11}^{\text{eff}}$ for model D and of $C_{11}^{\text{eff}}, C_{12}^{\text{eff}}, C_{22}^{\text{eff}}$ for model E show that GMC

![Figure 5.9. Stress-bridging paths for Model C.](image-url)
can capture the effect of stress-bridging, provided there are continuous rows of particles with edge-to-edge contacts extending completely across the RVE.

These studies of stress-bridging explain why GMC underestimates the effective modulus of the PBX 9501 models shown in Figure 5.5. In all these models, if 100×100 subcells are used to discretize the RVE, there are no rows or columns of subcells extending across the RVE that contain no binder. Though corner contacts and other continuous stress paths exist in the PBX 9501 models, the effects of these stress-bridging paths are not incorporated into the GMC estimates of effective stiffness. The strain-compatible or shear-coupled method of cells [82, 83] approaches may be able to overcome some of these deficiencies of GMC. However, the computational efficiency of GMC is greatly reduced when these modifications are incorporated into GMC and hence the attractiveness of this micromechanics approach as an alternative to finite element analysis is also reduced.

5.7 Summary and conclusions

The generalized method of cells (GMC) has been found to accurately predict the effective elastic properties of composites containing square arrays of disks for volume fractions up to 0.60. However, for two-dimensional models of the polymer bonded explosive PBX 9501, estimates of effective elastic properties from GMC have been found to be considerably lower than both experimental values and estimates based on finite element (FEM) calculations.

The lower values of normal stiffness predicted by GMC for PBX 9501 are due to inadequate incorporation of particle stress bridging into the approach. Model representative volume elements (RVEs) with corner and edge stress bridging show that corner bridging is ignored by GMC while edge stress bridging is incorporated only if continuous stress bridges exist along entire rows or columns of subcells that traverse the length of the RVE. Low values of effective shear stiffness predicted by GMC can be attributed to the use of a harmonic mean of subcell shear stiffnesses to determine the effective shear stiffness of a RVE. The harmonic mean is a lower bound on the effective shear stiffness and is not applicable for microstructures where there is significant interaction between
particles.

Improvements suggested to GMC that incorporate normal-shear coupling and strain compatibility across subcells have the potential to overcome some of these weaknesses of GMC. However, these improvements lead to much larger systems of equations and a considerable increase in the computational cost of the method. The requirement of inverting a large matrix to obtain the effective properties makes the generalized method of cells very inefficient as the number of subcells increases. When materials such as PBX 9501 are modeled, the number of subcells needed to represent a random distribution of particles necessarily becomes large. In such situations, the generalized method of cells becomes inefficient and it may be preferable to perform finite element analyses to determine the effective properties. Thus, GMC does not appear to be an improvement over finite element analyses for high volume fraction, high modulus contrast particulate composites such as polymer bonded explosives.
CHAPTER 6

ON PREDICTING THE EFFECTIVE ELASTIC PROPERTIES OF POLYMER BONDED EXPLOSIVES USING THE RECURSIVE CELL METHOD

6.1 Abstract

Polymer bonded explosives are particulate composites containing elastic particles in a viscoelastic binder. The particles occupy an extremely high fraction of the volume, often greater than 90% of the volume. Under low strain rate loading and at room temperature and higher, the elastic modulus of the particles can be four orders of magnitude higher than that of the binder. Rigorous bounds and analytical estimates for the effective elastic properties of these materials are inaccurate. Detailed numerical simulations can be computationally expensive because of the necessity of a high level of discretization of the microstructure. A fast real-space renormalization group method, called the recursive cell method, is explored in the context of the particulate composites and the high volume fraction, strong modulus contrast explosive PBX 9501. Results show that the recursive cell method overestimates the effective properties of particulate composites and PBX 9501 unless large blocks of subcells are renormalized and the particles in a representative volume element are randomly distributed. Percolation studies for strong modulus contrast particulate composites using the recursive cell method show an easily identifiable percolation threshold and critical exponent. However, the threshold and critical exponent are different from the finite element calculation based estimates and considerably lower than known values for elastic networks.
6.2 Introduction

One of the goals of multiscale modeling of materials is to predict the behavior of these materials across many different length scales. These length scales range from the atomistic (nanometers) to the macroscopic (meters). Many multiscale simulations move from a smaller scale to a larger one by using coarse-grained representations of the material and its microstructure in the larger scale. For example, molecular dynamics based estimates of the elastic properties of the components of a composite can be “coarse-grained” into a continuum description of the composite. Micromechanics provides a process by which “coarse-graining” can be achieved by producing effective properties that can be used in the macroscopic simulations.

For many composite materials, the effective elastic properties can be determined to excellent approximation by rigorous bounds or analytical approximations. However, polymer bonded explosives (PBXs) can have extremely high volume fractions of particles (> 0.9) and high modulus contrasts between particles and binder (> 20,000). Third-order bounds of effective moduli can be three orders of magnitude apart under these circumstances and analytical estimates can be an order of magnitude different from experimental values. Numerical simulations that explicitly consider the microstructure are therefore necessary for the prediction of effective properties of PBXs.

Direct numerical simulations can be quite computationally expensive. Methods derived from the real-space renormalization group [101, 102] provide a faster means of determining the effective properties of materials. The recursive cell method (RCM) is a computationally inexpensive renormalization-based approach for determining the effective elastic properties of a composite. The method has been developed as a substitute for detailed numerical analyses of high volume fraction and high modulus contrast particulate composites such as polymer-bonded explosives (PBXs). In the recursive cell method, the components of the composite are initially distributed in subcells in a regular grid. Small blocks of subcells are then homogenized in a recursive manner until an effective property of the composite is obtained. The homogenization of blocks of subcells is performed using finite elements.

Real-space renormalization approaches have been used by researchers to determine
the effective conductance of lattices [103] and composites [104], the effective permeability of rocks [105], effective dispersivities of flows [106], the effective hydraulic conductivity of heterogeneous media [107, 108], and the effective elastic properties of porous media [109]. No real-space renormalization approaches for the determination of effective elastic properties of composites have been found in the literature. However, such techniques have been for percolating elastic networks [110] that are used to study gel formation.

In this work, the recursive cell method is discussed and estimates of effective properties from this method are compared with estimates from finite element simulations for a range of volume fractions and modulus contrasts. The method is then applied to the polymer bonded explosive PBX 9501. The effect of increasing the number of subcells in a block during the homogenization process is also explored. Finally, the recursive cell method is applied to explore the behavior of high modulus contrast particulate composites near the “percolation threshold” where the effective modulus increases rapidly for small increases in particle volume fraction.

### 6.3 Background

Polymer bonded explosives are particulate composites containing a high volume fraction of explosive particles coated and supported by a binder. Some typical polymer bonded explosives are shown in Table 6.1. It can be seen that the particle volume fraction in each of these materials is extremely high. The explosive particles are linear elastic at or below room temperature. The binder is viscoelastic at room temperature. The modulus contrast between particles and the binder is high, especially close to and above room temperature.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PBX 9010</td>
<td>RDX</td>
<td>0.87</td>
<td>KEL-F-3700</td>
<td>0.13</td>
</tr>
<tr>
<td>PBX 9501</td>
<td>HMX</td>
<td>0.92</td>
<td>Estane 5703 + BDNPA/F</td>
<td>0.08</td>
</tr>
<tr>
<td>PBX 9502</td>
<td>TATB</td>
<td>0.90</td>
<td>KEL-F-800</td>
<td>0.10</td>
</tr>
</tbody>
</table>
PBX 9501 is a polymer bonded explosive containing monoclinic crystals of HMX (High Melting Explosive) dispersed in a viscoelastic binder which is a 1:1 mixture of a rubber (Estane 5703) and a plasticizer (bis-dinitropropylacetal/formal - BDNPA/F). Since the HMX crystals are randomly oriented in PBX 9501, isotropic elastic properties can be used while modeling the particles in the composite. Experiments on HMX [14] show an average Young’s modulus \((E)\) of 15.3 GPa and a Poisson’s ratio \((\nu)\) of 0.32. Molecular dynamics simulations [15] predict a Young’s modulus of 17.7 GPa and a Poisson’s ratio of 0.21 for HMX. Experiments on the binder in PBX 9501 show temperature and strain rate dependence of elastic properties. The binder has a Young’s modulus of approximately 0.7 MPa to 1 MPa at low strain rates [19]. The Young’s modulus of HMX is around 20,000 times that of the binder at these strain rates. At high strain rates, the Young’s modulus of HMX is around 10 to 20 times that of the binder. The binder modulus decreases with increase in temperature. Since the binder is rubbery, it is assumed to have a Poisson’s ratio of 0.49. The Young’s modulus of PBX 9501 at low strain rates is approximately 1 GPa, and at high strain rates around 5 to 7 GPa [4]. The Poisson’s ratio of PBX 9501 is around 0.35 [8].

Table 6.2 shows third-order bounds and some analytical estimates for the effective bulk and shear moduli of PBX 9501 at low strain rate and room temperature. Rigorous third-order bounds [23] on the effective elastic properties of PBX 9501 at low strain rates have been found to be considerably far apart. Commonly used analytical approximations such as the differential effective medium approximation (DEM) and the self-consistent scheme (SCS) [28] also provide inaccurate estimates for the elastic moduli of PBX 9501.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Modulus (MPa)</th>
<th>Shear Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBX 9501 (Experiments) [4, 8]</td>
<td>1100</td>
<td>400</td>
</tr>
<tr>
<td>Third-order Upper Bound [23]</td>
<td>11300</td>
<td>5000</td>
</tr>
<tr>
<td>Third-order Lower Bound [23]</td>
<td>220</td>
<td>70</td>
</tr>
<tr>
<td>Differential Effective Medium [28]</td>
<td>230</td>
<td>80</td>
</tr>
<tr>
<td>Self-Consistent Scheme [28]</td>
<td>11050</td>
<td>4700</td>
</tr>
</tbody>
</table>
Numerical determination of the effective properties of particulate composites involves the calculation of the stress and strain fields for a representative volume element (RVE) that simulates the microstructure of the composite. These stresses and strains are averaged over the volume \( V \) of the RVE and the effective elastic stiffness tensor \( C_{ijkl}^{\text{eff}} \) of the composite can be calculated from the tensor relation

\[
\int_V \sigma_{ij} dV = C_{ijkl}^{\text{eff}} \int_V \epsilon_{kl} dV,
\]

where \( \sigma_{ij} \) are the stresses and \( \epsilon_{ij} \) are the strains. The superscript 'eff' indicates an effective property. Estimates of the effective properties of PBX 9501 from finite element simulations show that the predicted properties are strongly dependent on microstructure and discretization (Chapter 4). Therefore, accurate prediction of the effective properties of PBX 9501 using finite elements requires extremely large meshes for accurate resolution of the microstructure and hence considerable computational resources.

An alternative to direct finite element simulation of PBX microstructures is the generalized method of cells [76]. In this method, a representative volume element is divided into a grid of subcells and equilibrium and compatibility are satisfied on an average basis across subcells. The effective stiffness matrix of the composite is determined directly from the average stress-strain relations after one matrix inversion. Though this method is more computationally efficient than finite element analyses for certain composites, it has been found to be relatively computationally expensive and inaccurate for large volume fraction, strong modulus contrast composites (Chapter 5).

Real-space renormalization group methods [101] are considerably faster than conventional averaging methods because the whole domain is not homogenized at a time. Instead, some averaging is done at a lower length scale and the average properties are re-normalized so that they can be used at a higher length scale. The recursive cell method follows this approach and has been developed so that the effective properties of finely discretized spatial domains can be calculated efficiently.

### 6.4 The recursive cell method

A schematic of the recursive cell method (RCM) is shown in Figure 6.1(a). In the recursive cell method, the RVE is discretized into a regular grid of subcells. The
subcells are assigned material properties depending on the particle distribution in the RVE. The subcells in the original grid are grouped into blocks of $n \times n$ subcells. The effective elastic stiffness matrix of each of the blocks is calculated using a finite element based approach. These stiffnesses are then assigned to a new, coarser grid. In standard renormalization approaches, this procedure is repeated until a “fixed point” is arrived at where the effective properties are constant. In these simulations, the domain is finite and hence the recursion terminates when only one homogeneous block remains after a number of iterations. The properties of this homogeneous block are the effective properties of the RVE.

An example of the RCM procedure is shown in Figure 6.1(b). The RVE is divided into a grid of subcells in such a way that each subcell contains only one material and the number of subcells per side of the ensemble is an integer factor of 2. The first iteration is carried out with the four subcells around the nodes marked 1. This leads to homogenized blocks that are used in the second iteration with the composite subcells around the nodes

![Figure 6.1](image_url)
marked 2. The final iteration shown in the figure is for the four composite blocks that make up the RVE at this stage. Homogenization of the final block gives the effective properties of the RVE.

A two-dimensional, plane-strain, finite element based approach that avoids numerical integration is used in the current implementation of RCM. Since renormalization-based approaches are quite sensitive to approximation errors [108] both four-noded displacement based elements and nine-noded displacement based elements, and nine-noded mixed displacement/pressure based elements have been implemented. Explicit forms of the strain-displacement and stress-strain relations are used to arrive at explicit forms for element stiffness matrices and average element stresses and strains. The explicit stiffness matrices for four- and nine-noded displacement based elements, and for nine-noded mixed displacement/pressure based elements are shown in Appendix B. Each subcell in a block is modeled using one finite element in the current implementation. Improved numerical accuracy can be achieved at the cost of computational efficiency if each subcell is further discretized.

Figure 6.2 shows a schematic of the normal displacement boundary conditions used to calculate the stresses and strains in a block of subcells. Uniform displacements are applied in one direction and periodicity of displacements is enforced in the block. Details of the manner in which boundary conditions are applied are discussed in Appendix C. The average stresses and strains in a block of subcells are then used to determine the

![Figure 6.2](image_url). Schematic of normal displacement boundary conditions in used RCM.
effective stiffness matrix of the block that is of the form

\[
C = \begin{bmatrix}
C_{11}^{\text{eff}} & C_{12}^{\text{eff}} & 0 \\
C_{12}^{\text{eff}} & C_{22}^{\text{eff}} & 0 \\
0 & 0 & C_{66}^{\text{eff}}
\end{bmatrix}.
\]  

(6.2)

After the whole RVE has been homogenized, the approximate effective two-dimensional Young’s modulus \(E_{\text{eff}}^{2\text{D}}\) and Poisson’s ratio \(\nu_{\text{eff}}^{2\text{D}}\) can be calculated using the relations

\[
\nu_{\text{eff}}^{2\text{D}} = \frac{2C_{12}^{\text{eff}}}{(C_{11}^{\text{eff}} + C_{22}^{\text{eff}})}
\]

(6.3)

\[
E_{\text{eff}}^{2\text{D}} = 0.5(C_{11}^{\text{eff}} + C_{22}^{\text{eff}})[1 - (\nu_{\text{eff}}^{2\text{D}})^2].
\]

(6.4)

A discussion of two- and three-dimensional elastic moduli is given in Appendix A. The three-dimensional Young’s modulus \(E_{\text{eff}}\) and Poisson’s ratio \(\nu_{\text{eff}}\) can be calculated from the two-dimensional moduli using [31]

\[
\nu_{\text{eff}} = \frac{\nu_{\text{eff}}^{2\text{D}}}{(1 + \nu_{\text{eff}}^{2\text{D}})}
\]

(6.5)

\[
E_{\text{eff}} = E_{\text{eff}}^{2\text{D}}[1 - (\nu_{\text{eff}})^2].
\]

(6.6)

The procedure used to calculate the average element stresses and strains and the effective properties a block of subcells is shown in Appendix D. Extension of the RCM technique to three dimensions follows the same procedure and is straightforward.

### 6.5 Models of particulate composites

Figure 6.3 shows representative volume elements, in two dimensions, of particulate composites containing 10% to 92% by volume of circular particles. The size distribution of the particles is roughly based on the particle size distribution of HMX in PBX 9501 [17]. Estimates of the effective three-dimensional Young’s modulus of these RVEs were obtained using the recursive cell method. Each RVE was discretized into \(256 \times 256\) subcells. A subcell was assigned particle properties if the total volume fraction of particles in the element was found to exceed 0.5 and binder properties otherwise. In the RCM calculations, each subcell was modeled using a nine-noded square displacement based element. A set of estimates of the effective Young’s modulus was obtained using blocks of \(2 \times 2\) subcells. The number of subcells in a block was then increased to \(16 \times 16\) and another set of estimates of Young’s modulus was calculated. The Young’s modulus
Figure 6.3. Nine RVEs containing 10% to 92% by volume of circular particles. \( f_p \) is the volume fraction of particles in a RVE.

and Poisson’s ratio used for the particles in the simulations were 100,000 MPa and 0.2 respectively. The Young’s modulus of the binder was varied from 1 MPa to 10 000 MPa in multiples of 10 and the Poisson’s ratio was kept fixed at 0.49.

Finite element analyses using 256×256 four-noded elements were also performed to determine the effective properties of the nine RVEs. Elements were assigned materials using the approach used in the RCM calculations. Periodic displacement boundary conditions were used to determine the average stresses and strains and the effective properties were calculated under plane-strain conditions.

Figure 6.4(a) shows recursive cell method (RCM) estimates of Young’s moduli of the nine RVEs in Figure 6.3 using blocks of 2×2 subcells. The finite element (FEM) estimates are shown in solid lines in the figure. Figure 6.4(b) shows RCM estimates using blocks of 16×16 subcells and the corresponding FEM estimates. The RCM estimates
Figure 6.4. Comparison of finite element (FEM) and RCM predictions for a range of modulus contrasts and volume fractions. $E_b$ is the Young’s modulus of the binder.
from calculations using 2×2 subcells per block are higher than the FEM estimates for all volume fractions and modulus contrasts shown in Figure 6.4(a). When the number of subcells in a block is increased to 16×16, the RCM estimates are closer to the FEM estimates. However, the RCM estimates of Young’s modulus are still considerably higher than the FEM estimates. These results indicate that the use of a finite element approach for determining the effective properties of a block of subcells in RCM leads to overestimation of the effective properties of the RVE. However, when harmonic means of the subcell properties are used as effective properties of a block of subcells (as has been done for conductivity problems [104]) considerably lower values of effective properties are obtained than from the FEM estimates.

6.6 Models of PBX 9501

A sample microstructure of PBX 9501 is shown in Figure 6.5. The particles in the microstructure are irregularly shaped and of a large number of sizes. The volume fraction of particles in PBX 9501 is around 92%. A digital image of the microstructure is difficult to simulate since particles and binder are not easily distinguished. Instead, models containing circular particles with particle size distributions that correspond to that of PBX 9501 have been used to model the polymer bonded explosive.

![Figure 6.5. Microstructure of PBX 9501 (adapted from [18]).](image)
Four microstructures based on the particle size distribution of the dry blend are shown in Figure 6.6(a). The microstructures contain 100, 200, 300 and 400 particles respectively. The corresponding RVE sizes are 0.65 mm, 0.94 mm, 1.13 mm and 1.325 mm. The particles in the microstructures occupy about 86% of the volume. Since actual PBX 9501 contains 92% particles, the remainder of the particle volume fraction is incorporated into a dirty binder. The dirty binder in the models shown in Figure 6.6(a) contains about 30% fine HMX particles and 70% binder. Microstructures based on the particle size distribution of pressed PBX 9501 are shown in Figure 6.6(b). The pressing process causes particle breakage and leads to a large volume fraction of smaller sized particles and fewer larger sized particles. The four microstructures shown in Figure 6.6(b) contain

![Figure 6.6. Model microstructures representing PBX 9501. (a) Four microstructures based on the dry blend of PBX 9501. (b) Four microstructures based on the size distribution of pressed PBX 9501.](image-url)
100, 200, 500, and 1000 particles respectively. The corresponding RVE sizes are 0.36 mm, 0.42 mm, 0.535 mm, and 0.68 mm. A dirty binder is also used in the simulation of these models. The elastic properties of HMX and binder at room temperature and low strain rate were used to calculate the effective properties of the eight RVEs. The differential effective medium approach was used to determine the elastic properties of the dirty binder.

The model RVEs in Figure 6.6 were discretized into 256×256 subcells. Effective properties of these RVEs were calculated with RCM using blocks of 2×2 subcells each modeled with a four-noded element. For the first recursion, subcells containing more than 50% binder were assigned dirty binder properties while those containing less than 50% binder were assigned particle properties. Figure 6.7(a) shows the effective Young's moduli of the model RVEs and Figure 6.7(b) shows the Poisson’s ratios from RCM calculations. Estimates from finite element simulations of the RVEs are also shown in the figure. The experimentally determined Young’s modulus and Poisson’s ratio of PBX 9501 are also shown for comparison. The values of Young’s modulus predicted by RCM are almost an order of magnitude higher than the experimental value for PBX 9501. The RCM estimates are also more than double the FEM estimates for most of the RVEs. The Poisson’s ratio of PBX 9501 is underestimated by RCM by a factor of 2.

Both four-noded and nine-noded displacement based elements predicted approximately the same effective moduli when used to model the subcells in RCM. Hence, an increase in the number of degrees of freedom did not lead to a significant decrease in the stiffness predicted by RCM. Nearly incompressible materials such as the binder can cause element locking [87]. To avoid such locking, the binder subcells were then modeled with nine-noded mixed displacement-pressure elements. Use of these mixed elements was also observed not to cause any significant lowering of the estimated Young’s modulus. A possible source of error in the estimates is that only four elements are used to model a block of 2×2 subcells containing materials of strong modulus contrast. An investigation has shown that if 1000 elements are used to model a block of four subcells, the estimated effective Young’s modulus is about half of that obtained when four elements were used. However, such high refinement is not allowable in the interest
Figure 6.7. Effective elastic properties of models of PBX 9501 from RCM calculations.

of computational efficiency. The simulations of the models shown in Figure 6.3 show that improved estimates are obtained if the number of subcells in a block is increased. This option is explored further for the two models of PBX 9501 shown in Figure 6.8.

Figure 6.8(a) shows a manually generated RVE (Model A) containing 92% particles by volume. Figure 6.8(b) shows an automatically generated RVE (Model B) containing 86% particles by volume and a dirty binder. Both RVEs represent PBX 9501. A set of RCM simulations were performed on these microstructures with increasing subcells per block using nine-noded displacement based elements after discretizing each into 256×256 subcells. Material properties of the components of PBX 9501 at room temperature and low strain rate were used to determine the composite properties.

Figure 6.9(a) shows the convergence of the RCM estimates towards the finite element estimates with increase in the number of subcells per block (in the first step of recursion). For the manually generated model (Model A), the RCM estimates are around 4 times higher than the FEM estimates when 2×2 subcells per block are used. The RCM estimates get closer to the FEM estimates when the subcells per block are increased. However, the RCM predictions always remain at least three times higher than the FEM
Figure 6.8. High volume fraction model microstructures. (a) Manually generated microstructure with 92% by volume of particles. (b) Automatically generated microstructure with 86% by volume of particles.

estimates. A much better convergence to the FEM model is obtained for Model B. The RCM estimates are within 10% of the FEM estimates when $32 \times 32$ subcells are used per block. The reason for the improved convergence is probably because the particles are randomly distributed in Model B and errors are averaged out in each recursion while the pattern of particles in Model A does not allow such averaging to occur.

Figure 6.9(b) shows the CPU times taken to determine the RCM estimates for Model A compared to the time taken for the detailed finite element simulations on a Sun Ultra Sparc 60 processor. Note that these CPU times do not reflect efficiencies that are achieved by avoiding redundant calculations for identical blocks or blocks containing only particles or binder. It can be seen that the time taken for the RCM calculations is always lower than the time taken for the FEM simulation irrespective of the number of subcells used to form a block. This is encouraging because it implies that parallel simulations with the RCM approach can achieve good computational efficiency. The drop in the CPU time for the $64 \times 64$ subcells per block case can probably be attributed to the microstructure of Model B where large blocks of subcells are filled only with particles and hence require no computation.

Comparisons of total strain energy densities of the RVE at each level of recursion in
Figure 6.9. RCM estimates of Young’s modulus with increasing subcells per block and the CPU time taken.

RCM also show a similar decrease to a relatively steady value with increase in the number of subcells in a block. Figure 6.10(a) shows the decrease in strain energy density with increase in the number of subcells per block. The data presented are for a uniform normal strain of 0.01 mm/mm. The data point in the figure that corresponds to 65,536 subcells per block is from direct finite element calculations with $256^2$ elements. For Model A the total strain energy from RCM calculations decreases by a factor of 2 with increasing subcells per block but remains around 5 times higher than the strain energy from the finite element calculation. For Model B, the strain energy starts at around 1.5 the finite element based value and converges rapidly towards that value. This implies that the larger the gap in the strain energy from 2×2 RCM calculations and the full FEM calculations, the smaller the chance that convergence to an accurate estimate will be obtained with increase in the number of subcells per block. However, this information cannot be used without a-priori knowledge of the finite element estimate. If the reduction of strain energy density with the number of recursions is considered (as shown for Model B in Figure 6.10(b)) it is observed that the strain energy density decreases with each recursion instead of remaining constant. This reduction is also not large enough to approach the
FEM estimate (labeled 256×256 in the figure) when small numbers of subcells are used per block. These results show that RCM estimates can be quite different from FEM estimates for the same amount of discretization of the RVE unless large blocks of subcells are homogenized at each level of recursion. It also appears that the strain energy density cannot be used to determine the appropriate number of subcells per block to be used at a level of recursion for improved accuracy.

### 6.7 Percolation

Renormalization-based techniques have been widely used for studying critical behavior in percolating systems [110, 111]. For elastic materials, an example of such a system that contains randomly distributed solid particles surrounded by a fluid. Below a certain threshold volume fraction of particles, called the critical volume fraction \( p_c \) the material behaves like a fluid. Above \( p_c \) continuous regions of particles develop that lead to solid like behavior in the material as in gels. Studies on two-dimensional elastic networks [112] have found that the bulk and shear moduli of these networks above the
critical point are related to the volume fraction of solids \((p)\) by a power law of the form

\[ K, G \propto (p - p_c)^T \tag{6.7} \]

where \(K\) is the bulk modulus, \(G\) is the shear modulus and \(T\) is the critical exponent.

For two-dimensional elastic networks, the value of \(p_c\) is about 0.58 and the value of \(T\) is around 3.5 to 3.9 \([110, 113]\). In this section, the critical exponent of PBX-like materials is evaluated in two dimensions.

At and above room temperature and at low strain rates, polymer bonded explosives such as PBX 9501 can have components with a modulus contrast of around 25,000. Since the binder is viscous at these temperatures, unless a sufficiently large volume fraction of particles is added to the binder it has a tendency to relax rapidly. Thus, PBX materials are similar to gels and amenable to studies of percolation behavior. RCM simulations have been performed on 95 two-dimensional RVEs similar to those shown in Figure 6.3 for various volume fractions of particles. As before, each RVE was divided into 256x256 subcells and 2x2 subcells were used to form a block. The particles were assigned a Young’s modulus of 25,000 MPa and a Poisson’s ratio of 0.2 while the binder was assigned a Young’s modulus of 1 MPa and a Poisson’s ratio of 0.49.

Figure 6.11(a) shows the RCM estimates of effective two-dimensional bulk modulus as a function of particle volume fraction \((p)\). The figure shows that the effective bulk modulus is small for volume fractions less than around 0.63 after which there is a rapid increase in the values. If the critical point is taken to be \(p_c = 0.63\) and the bulk modulus is plotted against \(p - p_c\) as shown in Figure 6.11(b), a critical exponent of \(T = 1.18\) is obtained from a least squares fit to the data. This exponent is about half the value reported for two-dimensional elastic networks \([110]\). The estimated Young’s modulus for a particle volume fraction of 0.92 is around 10,900 MPa using the power law obtained from the RCM calculations. This is around 10 times the Young’s modulus of PBX 9501.

On the other hand, if finite element estimates for the same RVEs with the same level of discretization are observed, the percolation behavior is quite different as can be seen in Figures 6.12(a) and 6.12(b). In this case, the critical exponent is found to be even lower,
Figure 6.11. Percolation behavior in high modulus contrast composites from RCM calculations. (a) Effective two-dimensional bulk modulus vs. volume fraction ($p$). (b) Effective two-dimensional bulk modulus vs. $p - p_c$.

Figure 6.12. Percolation behavior in high modulus contrast composites from FEM calculations. (a) Effective two-dimensional bulk modulus vs. volume fraction ($p$). (b) Effective two-dimensional bulk modulus vs. $p - p_c$. 
about 0.77 and the percolation threshold is around 0.78. If the power law obtained from the FEM calculations is used to calculate the effective two-dimensional Young’s modulus at a volume fraction of 0.92, an estimate of 1,654 MPa is obtained. This estimate is quite close to the experimentally determined value of Young’s modulus of PBX 9501. This result suggests that simulations of systems at lower volume fractions can be used to determine the effective properties of high volume fraction composites above the critical threshold. However, a renormalization-based approach such as RCM may not be accurate enough for that purpose. The rapid increase in the elastic modulus beyond the critical point shows that stress bridging begins to play an important role in determining effective elastic properties beyond this point. The critical exponent can be used as a parameter that quantifies the amount of stress bridging in a high volume fraction particulate composite.

6.8 Summary and conclusions

Rigorous bounds and analytical approximations for the effective elastic properties of polymer bonded explosives generate inaccurate estimates because of the high volume fraction of particles and the strong modulus contrast in these composites. Numerical approximations using the finite element method are computationally intensive for the same reasons. The renormalization-based recursive cell method was developed so that effective elastic moduli of these composites could be obtained at low computational expense. A finite element method was used to determine the effective properties of blocks of subcells in each recursion.

Using the recursive cell method, estimates of effective elastic properties for various microstructures are found to be higher than predictions from finite element calculations for a range of volume fractions and modulus contrasts. Improved estimates are obtained when the number of subcells in a renormalization block is increased. However, the improvement in the predicted elastic moduli depends strongly on the geometry of the microstructure being modeled. Better estimates are obtained if the particle distribution is random. The percolation behavior of models of particulate composites with strong modulus contrast indicates that there is a clearly demarcated critical point and an identifiable critical exponent for these materials. Finite element and recursive cell method
calculations provide two different critical particle volume fractions and critical exponents that are considerably lower than known values for elastic networks. More simulations may be required to accurately quantify these parameters for strong modulus contrast polymer bonded explosives.

These results suggest that renormalization approaches that use finite elements to homogenize blocks of subcells overestimate the effective properties of particulate composites when compared to direct finite element calculations. Therefore, even though these methods can be considerably faster than direct numerical simulations, they are not recommended for high volume fraction and strong modulus contrast particulate composites. An alternative to using finite element methods for homogenization of blocks could be to use a method such as the generalized method of cells that tends to underestimate effective properties. Thus, the inherent tendency of overestimation by the renormalization approach could be balanced by a method that underestimates block properties leading to better estimates of effective elastic properties.
CHAPTER 7

ON EXACT RELATIONS FOR THE
CALCULATION OF EFFECTIVE
ELASTIC PROPERTIES OF
COMPOSITES

7.1 Abstract

Numerous exact relations exist that relate the effective elastic properties of composites to the elastic properties of their components. These relations can not only be used to determine the properties of certain composites, but also provide checks on the accuracy of numerical techniques for the calculation of effective properties. In this work, some exact relations are discussed and estimates from finite element calculations, the generalized method of cells and the recursive cell method are compared with estimates from the exact relations. Comparisons with effective properties predicted using exact relations show that the best estimates are obtained from the finite element calculations while the moduli are overestimated by the recursive cell method and underestimated by the generalized method of cells. Some exact relations are found to be more suitable than others for determining the relative accuracy of various numerical methods.

7.2 Introduction

Exact relations for the effective elastic properties of two-component composites can be classified into three types. The first type consists of relations that have been determined from the similarity of the two-dimensional stress and strain fields for certain types of materials. These exact relations are called duality relations [114]. The second type of exact relations, called translation-based relations, state that if a constant quantity is added to the elastic moduli of the component materials then the effective elastic moduli are also “translated” by the same amount. Microstructure independent exact relations,
valid for special combinations of the elastic properties of the components, form the third category [115]. The known exact relations are directly applicable to only a limited range of properties of the components. Therefore the utility of these relations lies not only in determining the effective elastic properties of a small range of composites but also in evaluating the accuracy of numerical and analytical methods of computing effective properties. In this work, predictions from exact relations are compared with estimates from finite element calculations, the generalized method of cells (GMC) [76], and the recursive cell method (RCM). The goal is to assess the effectiveness of these relations in evaluating the accuracy of the three numerical methods, especially with regard to high modulus contrast materials such as polymer bonded explosives.

Five exact relations are explored in this work. The first is a duality-based identity for the effective shear modulus that is valid for phase-interchangeable materials [32]. The second is a set of duality relations that are valid for materials that are rigid with respect to shear [114]. Two translation-based relations are explored next: the Cherkaev-Lurie-Milton (CLM) theorem [116] and a relation for symmetric composites with equal bulk modulus [32]. Finally, the microstructure independent Hill’s relation [117] is explored.

### 7.3 Phase interchange identity

A symmetric composite is one that is invariant with respect to interchange of the components. A checkerboard, as shown in Figure 7.1, is an example of a symmetric composite. The phase interchange identity [32] for the effective shear modulus of a symmetric two-dimensional two-component isotropic composite is a duality-based exact relation that states that

\[
G_{\text{eff}} = \sqrt{G_1 G_2}
\]

(7.1)

where \(G_1, G_2\) are the shear moduli of the two components and \(G_{\text{eff}}\) is the effective shear modulus.

The phase interchange identity is valid for macroscopically isotropic composites. In a finite-sized representative volume element (RVE) for a checkerboard composite the shear modulus is not the same all directions and hence isotropy is not achieved. The
two-dimensional stress-strain relation for such a RVE with “square symmetry” can be written as

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{12}
\end{bmatrix} = \begin{bmatrix}
K + \mu^{(1)} & K - \mu^{(1)} & 0 \\
K - \mu^{(1)} & K + \mu^{(1)} & 0 \\
0 & 0 & \mu^{(2)}
\end{bmatrix} \begin{bmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
2\langle \epsilon_{12} \rangle_V
\end{bmatrix}
\] (7.2)

where \(\sigma_{11}, \sigma_{22}, \sigma_{12}\) are the stresses,
\(\epsilon_{11}, \epsilon_{22}, \epsilon_{12}\) are the strains,
\(K\) is the two-dimensional bulk modulus,
\(\mu^{(1)}\) is the shear modulus for shear along the diagonals of the RVE, and
\(\mu^{(2)}\) is the shear modulus for shear along the edges of the RVE.

The numerical verification of the phase interchange identity requires that the components of the composite be chosen so that the difference between \(\mu^{(1)}\) and \(\mu^{(2)}\) for the composite is minimal. This implies that the components should have a weak modulus contrast.

Numerical estimates of the effective elastic properties of the checkerboard composite shown in Figure 7.1 were obtained using finite elements (FEM), the recursive cell method (RCM) and the generalized method of cells (GMC). Following the requirement of low modulus contrast, both components were assigned a Young’s modulus of 15,300 MPa.
The Poisson’s ratio of the first component was fixed at 0.32 while that of the second component was varied from 0.1 to 0.49. The FEM calculations were performed using a mesh of $256 \times 256$ four-noded square elements. The RCM calculations used a grid of $64 \times 64$ subcells with blocks of $2 \times 2$ subcells and each subcell was modeled using one nine-noded element. The GMC calculations used $64 \times 64$ square subcells to discretize the RVE.

Figure 7.2 shows a comparison of the exact effective shear modulus for the checkerboard composite with estimates of $\mu^{(1)}$ and $\mu^{(2)}$ from the three numerical approaches. The results show that all the three methods perform well (the maximum error is 0.1%) in predicting the effective shear modulus when the modulus contrast is small, that is, when the composite is nearly isotropic. It can also be observed that the values of $\mu^{(1)}$ and $\mu^{(2)}$ are within 1% of each other for the chosen component moduli.

**Figure 7.2.** Validation of FEM, RCM and GMC using the phase interchange identity for a checkerboard composite.
7.3.1 Range of applicability

The question that arises at this point is whether the three numerical approaches can predict the phase interchange identity for larger modulus contrasts. Numerical calculations have been performed on the checkerboard microstructure to explore this issue. The first component of the checkerboard was assigned a Young’s modulus of 15,300 MPa and a Poisson’s ratio of 0.32. For the second component, the Poisson’s ratio was fixed at 0.49 and the Young’s modulus was varied from 0.7 MPa to 7000 MPa.

Figure 7.3 shows plots of the effective $\mu^{(1)}$ and $\mu^{(2)}$ versus shear modulus contrast for a checkerboard RVE. When the modulus contrast between the components of the checkerboard exceeds 2, the material can no longer be considered isotropic since the values of $\mu^{(1)}$ and $\mu^{(2)}$ are considerably different from each other. However, the values of $\mu^{(1)}$ predicted by FEM are quite close to the effective shear modulus $G_{\text{eff}}$ predicted by the phase interchange identity. This result suggests that the simulation of a diagonal shear may not be necessary to predict the effective shear modulus of an isotropic composite.

![Figure 7.3](image)

Figure 7.3. Variation of effective shear moduli with modulus contrast for a checkerboard composite.
composite when the finite element approach is used. This result also implies that the phase interchange identity can be used for a much larger range of modulus contrasts. The effective shear moduli predicted by GMC are considerably lower than that from the exact relation while the values from RCM are consistently higher. The RCM estimates worsen with increasing modulus contrast. If only the value of $\mu^{(1)}$ is examined, the phase interchange identity indicates that the FEM approach is much more accurate than the GMC and RCM approaches. However, it is difficult to choose between GMC and RCM for high modulus contrast composites. While the exact value of $\mu^{(1)}$ is 10 times the value predicted by GMC, the corresponding RCM estimate is 10 times the exact value. These results confirm the findings of detailed numerical studies on high modulus contrast, high volume fraction polymer bonded explosives (Chapters 4, 5, and 6).

The range of direct applicability of the phase interchange identity can be increased by using the Cherkaev-Lurie-Milton theorem to translate the original component properties. This theorem is discussed later in terms of its direct applicability to determining the accuracy of FEM, GMC and RCM.

### 7.3.2 Convergence of FEM calculations

The checkerboard material provides an extreme case to test the convergence of the FEM solution because the corner singularities lead to high stresses that can only be resolved with refined meshes. Figure 7.4 shows the convergence of the effective $\mu^{(1)}$ and $\mu^{(2)}$ with increasing mesh refinement for a checkerboard with a shear modulus contrast of about 25,000. The effective $\mu^{(1)}$ converges to a steady value when $128 \times 128$ elements are used to discretize the RVE. The shear modulus $\mu^{(2)}$ reaches a steady value when $256 \times 256$ elements are used. Based on this result, the finite element calculations in this work were performed using $256 \times 256$ elements or more.

RCM uses a finite element approach to homogenize blocks of subcells. When blocks of $2 \times 2$ subcells are used, some of these blocks can resemble checkerboards - especially at the first level of recursion for a two-component composite. The finite element convergence result suggests that RCM may overestimate the effective shear moduli by a factor of two if a block of four subcells is simulated using only four finite elements.
7.4 Materials rigid in shear

The stress-strain response of two-dimensional materials that are rigid with respect to shear can be represented by

\[
\begin{bmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
\epsilon_{12}
\end{bmatrix} =
\begin{bmatrix}
S_{11} & S_{12} & 0 \\
S_{12} & S_{22} & 0 \\
0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{12}
\end{bmatrix}.
\]

(7.3)

where \(\sigma_{11}, \sigma_{22}\) and \(\sigma_{12}\) are the stresses,

\(\epsilon_{11}, \epsilon_{22}\) and \(\epsilon_{12}\) are the strains, and,

\(S_{ij}\) are the components of the compliance matrix.

Two duality-based relations that are valid for two-component composites composed of such materials are [114]:

Relation RS1 If \(S_{11}S_{22} - (S_{12})^2 = \Delta\) for each phase (where \(\Delta\) is a constant), then the effective compliance tensor also satisfies the same relationship, i.e., \(S_{11}^{\text{eff}}S_{22}^{\text{eff}} - (S_{12}^{\text{eff}})^2 = \Delta_{\text{eff}}\). This relation is true for all microstructures.
Relation RS2 If the compliance tensors of the two phases are of the form $S_1 = \alpha_1 A$ and $S_2 = \alpha_2 A$ where $A$ is a constant matrix, then the effective compliance tensor of a checkerboard of the two phases satisfies the relation $\det S_{\text{eff}} = S_{11}^{\text{eff}} S_{22}^{\text{eff}} - (S_{12}^{\text{eff}})^2 = \alpha_1 \alpha_2 (A_{11} A_{22} - (A_{12})^2)$.

7.4.1 Relation RS1

Figure 7.5 shows a square array of disks occupying an area fraction of 0.7. Numerical experiments have been performed on this array of disks to check if Relation RS1 can be reproduced by finite element analyses, GMC and RCM. The $S$ matrices that have been used for the disks (superscript 1) and the matrix (superscript 2), and the corresponding values of $\Delta$ are shown below. These matrices have been chosen so that the value of $\Delta$ is constant.

$$S_1 = \begin{bmatrix} 1000 & -300 & 0 \\ -300 & 1000 & 0 \\ 0 & 0 & 0.001 \end{bmatrix}, \quad \Delta = 9.1 \times 10^5,$$

and

$$S_2 = \begin{bmatrix} 1094.3 & -536.21 & 0 \\ -536.21 & 1094.3 & 0 \\ 0 & 0 & 0.001 \end{bmatrix}, \quad \Delta = 9.1 \times 10^5.$$

Figure 7.5. RVE for a square array of disks.
The shear modulus for both materials is 1000 (arbitrary units) - around $10^6$ times the Young’s modulus. Higher values of shear modulus have been tested and found not to affect the effective stiffness matrix significantly.

Table 7.1 shows the values of $S_{11}^{\text{eff}}$, $S_{12}^{\text{eff}}$ and $\Delta_{\text{eff}}$ calculated using finite elements (350×350 elements), GMC (64×64 subcells) and RCM (256×256 subcells). The ratio of the calculated $\Delta_{\text{eff}}$ to the original $\Delta$ are also shown in the table. The modulus contrast between the two components of the composite is small, so the calculated effective properties are expected to be accurate (based on the results on the phase interchange identity for shear moduli). However, the results in Table 7.1 show that all three numerical methods predict values of $\Delta_{\text{eff}}$ that are around half the original $\Delta$. These results imply that all three methods (FEM, GMC and RCM) overestimate the effective normal stiffness of the array of disks. Relation RS1 for materials rigid in shear may therefore be a very sensitive test of the accuracy of numerical methods even though the modulus contrast that can be used is small.

### 7.4.2 Relation RS2

The second duality relation for materials that are rigid in shear requires that Relation RS2 is valid for the checkerboard geometry shown in Figure 7.1. The following values of the elastic properties have been used to test the accuracy of FEM, RCM and GMC in predicting this relation.

\[
S_1 = 100 \begin{bmatrix} 10 & -3 \\ -3 & 10 \end{bmatrix}; \quad S_2 = 1000 \begin{bmatrix} 10 & -3 \\ -3 & 10 \end{bmatrix}
\]

\[
\alpha_1 = 100; \quad \alpha_2 = 1000
\]

\[
A = \begin{bmatrix} 10 & -3 \\ -3 & 10 \end{bmatrix}
\]

### Table 7.1. Two-dimensional effective compliance matrix for a square array of disks.

<table>
<thead>
<tr>
<th></th>
<th>$S_{11}^{\text{eff}}$</th>
<th>$S_{12}^{\text{eff}}$</th>
<th>$\Delta_{\text{eff}} \left( \times 10^6 \right)$</th>
<th>$\Delta_{\text{eff}}/\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEM</td>
<td>850.35</td>
<td>-536.32</td>
<td>4.35</td>
<td>0.48</td>
</tr>
<tr>
<td>RCM</td>
<td>847.25</td>
<td>-538.17</td>
<td>4.28</td>
<td>0.47</td>
</tr>
<tr>
<td>GMC</td>
<td>871.75</td>
<td>-517.14</td>
<td>4.93</td>
<td>0.54</td>
</tr>
</tbody>
</table>
The duality relation requires that the effective compliance matrix of the checkerboard composite should be such that

$$\det(S_{\text{eff}}) = S_{11}^{\text{eff}}S_{22}^{\text{eff}} - (S_{12}^{\text{eff}})^2 = 9.10 \times 10^6.$$

The FEM calculations were performed using $350 \times 350$ four-noded elements, the RCM calculations used $64 \times 64$ subcells (blocks of $2 \times 2$ subcells) and the GMC calculations used $64 \times 64$ subcells too. The results from these three methods are tabulated in Table 7.2. The finite element calculations lead to an accurate effective compliance matrix that deviates from the exact result by only 25%. The GMC calculations overestimate the compliance matrix and the determinant of the compliance matrix is around 2.3 times higher than the exact result. However, the RCM calculations predict a compliance matrix that has a determinant that is only around 20% of the exact value.

### 7.5 The CLM theorem

The Cherkaev, Lurie and Milton (CLM) theorem is a well known “translation” based exact relation for two-component planar composites [116]. For a two-dimensional two-component isotropic composite, this theorem can be stated as follows:

**Theorem 7.1** Let the isotropic bulk moduli of the two components be $K_1$ and $K_2$.

Let the shear moduli of the two components be $G_1$ and $G_2$.

Let the effective bulk and shear modulus of a two-dimensional composite made of these two components be $K_{\text{eff}}$ and $G_{\text{eff}}$, respectively.

Let us now create two new materials that are translated from the original component materials by a constant amount $\lambda$. That is, let the bulk and shear moduli of the translated

<table>
<thead>
<tr>
<th></th>
<th>$S_{11}^{\text{eff}}$</th>
<th>$S_{12}^{\text{eff}}$</th>
<th>$\det(S_{\text{eff}})/(\times 10^6)$</th>
<th>$\det(S_{\text{eff}})/\alpha_1\alpha_2\det A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEM</td>
<td>3282</td>
<td>-2004</td>
<td>6.75</td>
<td>0.74</td>
</tr>
<tr>
<td>RCM</td>
<td>1655</td>
<td>-7090</td>
<td>2.23</td>
<td>0.24</td>
</tr>
<tr>
<td>GMC</td>
<td>5007</td>
<td>-2146</td>
<td>2.05</td>
<td>2.25</td>
</tr>
</tbody>
</table>
component materials be given by

\[
\begin{align*}
1/K_1^T &= 1/K_1 - \lambda; \quad 1/G_1^T = 1/G_1 + \lambda; \\
1/K_2^T &= 1/K_2 - \lambda; \quad 1/G_2^T = 1/G_2 + \lambda.
\end{align*}
\]

Then the effective bulk and shear moduli of a two-dimensional composite of the two translated materials, having the same microstructure as the original composite, are given by

\[
1/K_{\text{eff}}^T = 1/K_{\text{eff}} - \lambda; \quad 1/G_{\text{eff}}^T = 1/G_{\text{eff}} + \lambda. \tag{7.4}
\]

The requirement of isotropy can be satisfied approximately for numerical experiments by choosing component material properties that are very close to each other. Since our goal is to determine how well GMC and RCM perform for high modulus contrast, choosing materials with small modulus contrast is not adequate. Another alternative is to choose a RVE that represents a hexagonal packing of disks. However, such an RVE is necessarily rectangular and cannot be modeled using RCM in its current form. It should be noted that RCM can easily be modified to deal with elements that are not square and hence to model rectangular regions.

Another problem in the application of the CLM theorem is that the value of \(\lambda\) has to be small if the difference between the original and the translated moduli is large and vice versa. If the value of \(\lambda\) is small, floating point errors can accumulate and exceed the value of \(\lambda\). On the other hand, if \(\lambda\) is large, the original and the translated moduli are very close to each other and the difference between the two can be lost because of errors in precision. Hence, the numbers have to be chosen carefully keeping in mind the limits on the value of the Poisson’s ratio.

The translation relation has been tested on the square array of disks occupying a volume fraction of 0.70 from Figure 7.5. This RVE exhibits square symmetry, i.e., the shear moduli \(\mu^{(1)}\) and \(\mu^{(2)}\) shown in equation (7.2) are not equal. A unique value of the effective shear modulus cannot be calculated for this RVE. Instead, the value of the effective translated shear modulus is calculated from equation (7.4) by first setting \(G_{\text{eff}}\) equal to \(\mu^{(1)}\) and then to \(\mu^{(2)}\). These “exact” values are compared with the \(\mu^{(1)}\) and \(\mu^{(2)}\) values predicted using finite element analyses, GMC and RCM.
The original set of elastic moduli for the RVE is chosen to reflect the elastic moduli of the constituents of polymer bonded explosives. These moduli are then translated by a constant $\lambda = 0.001$. The original and the translated constituent two-dimensional moduli are shown in Table 7.3 (phase 'p' represents the particles and phase 'b' represents the binder). It can be observed that the translation process creates a large change in the bulk modulus of the particles. Table 7.4 shows the effective bulk and shear moduli of the original and the translated material calculated using finite elements ($350 \times 350$ elements), GMC ($64 \times 64$ subcells) and RCM ($256 \times 256$ subcells). The values of $\lambda_{\text{err}}$ shown in the table have been calculated using

$$\lambda_{\text{err}} = (\lambda/0.001 - 1) \times 100,$$

where,

$$\lambda = 1/K_{\text{eff}} - 1/K_{\text{eff}}^T = 1/\mu_{\text{eff}}^{(T)} - 1/\mu_{\text{eff}}^i.$$

Even though the modulus contrast between the two components of the composite is high, the effective properties predicted by FEM, GMC and RCM are close to each other in magnitude. The effective moduli of the translated composite are also close to that of

<table>
<thead>
<tr>
<th>Table 7.3. Original and translated two-dimensional constituent moduli for checking the CLM condition.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p$</td>
</tr>
<tr>
<td>(x10^2)</td>
</tr>
<tr>
<td>Original</td>
</tr>
<tr>
<td>Translated</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 7.4. Comparison of effective moduli for the original and the translated composites.</th>
</tr>
</thead>
</table>
| $K_{\text{eff}}$ | $\lambda_{\text{err}}$(%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FEM</td>
<td>36.4</td>
<td>37.8</td>
<td>-0.8</td>
<td>10.1</td>
<td>10</td>
<td>-3.1</td>
<td>0.9</td>
</tr>
<tr>
<td>RCM</td>
<td>42.5</td>
<td>44.5</td>
<td>6.1</td>
<td>29.8</td>
<td>29</td>
<td>-6.9</td>
<td>1.3</td>
</tr>
<tr>
<td>GMC</td>
<td>34.0</td>
<td>35.1</td>
<td>-1.3</td>
<td>3.8</td>
<td>3.8</td>
<td>5.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>
the original composite as predicted by the CLM condition. Interestingly, all the three methods satisfy the CLM condition and the error is small (as seen by the values of $\lambda_{err}$). Of the three methods, FEM and GMC produce the lowest error while RCM produces the highest error.

### 7.6 Composites with equal bulk modulus

The translation procedure can also be used to generate an exact solution for the effective shear modulus of two-dimensional symmetric two-component composites with both components having the same bulk modulus [32]. This relation is

$$
K_{\text{eff}} = K = K_1 = K_2
$$

$$
G_{\text{eff}} = \frac{K}{-1 + \sqrt{\left(1 + \frac{K}{G_1}\right) \cdot \left(1 + \frac{K}{G_2}\right)}}
$$  \hspace{1cm} (7.5)

This relation has been tested on the checkerboard model shown in Figure 7.1 using the component material properties given in Table 7.5. The exact effective properties for the composite, calculated using equation (7.5), are also given in the table. The values of the effective moduli calculated using finite elements (FEM), GMC and RCM are also shown in Table 7.5.

These results show that the effective two-dimensional bulk modulus is calculated correctly by all the three methods. However, the shear moduli calculated for the checkerboard microstructure are quite different from the exact result. This exact result also shows that the FEM calculations are the most accurate, followed by GMC and then RCM. The values of $\mu_{\text{eff}}^{(1)}$ are also found to most closely approximate the value of $G_{\text{eff}}$.

### 7.7 Hill’s equation

Hill’s equation [117] is an exact relation that is independent of microstructure. This equation is valid for composites composed of isotropic components that have the same shear modulus. For a two-dimensional two-component composite, this equation can be written as

$$
\frac{1}{K_{\text{eff}} + G} = \frac{f_p}{K_p + G} + \frac{f_b}{K_b + G}
$$  \hspace{1cm} (7.6)
Table 7.5. Component properties, exact effective properties and numerically computed effective properties for two-component symmetric composite with equal component bulk moduli.

<table>
<thead>
<tr>
<th>Component</th>
<th>$E$ ($\times 10^2$)</th>
<th>$\nu$</th>
<th>$K$ ($\times 10^3$)</th>
<th>$G$ ($\times 10^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component 1</td>
<td>25.00</td>
<td>0.25</td>
<td>2.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Component 2</td>
<td>1.19</td>
<td>0.49</td>
<td>2.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Composite</td>
<td>5.12</td>
<td>0.46</td>
<td>2.0</td>
<td>1.76</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$K_{\text{eff}}$ ($\times 10^2$)</th>
<th>$\mu_{\text{eff}}^{(1)}$ ($\times 10^2$)</th>
<th>Diff. %</th>
<th>$\mu_{\text{eff}}^{(2)}$ ($\times 10^2$)</th>
<th>Diff. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEM 20</td>
<td>1.29</td>
<td>-26.8</td>
<td>2.54</td>
<td>44.4</td>
</tr>
<tr>
<td>GMC 20</td>
<td>0.77</td>
<td>-56.3</td>
<td>0.77</td>
<td>-56.3</td>
</tr>
<tr>
<td>RCM 20</td>
<td>2.96</td>
<td>68.0</td>
<td>4.41</td>
<td>150.9</td>
</tr>
</tbody>
</table>

where $f$ represents a volume fraction, $K$ represents a bulk modulus, and $G$ represents a shear modulus. The subscript 'p' represents a particle property, 'b' represents a binder property, and 'eff' represents the effective property of the composite.

This relationship is verified using the RVE containing an array of disks occupying 70% of the volume that is shown in Figure 7.5. Table 7.6 shows the properties of the two components used to compare the predictions of finite elements, GMC and RCM with the exact value of bulk modulus predicted by Hill’s equation. It should be noted that the materials chosen are not representative of polymer bonded explosive materials.

Since the modulus contrast is small, the square array of disks is expected to exhibit nearly isotropic behavior. Therefore, the predictions of finite elements, GMC and RCM are expected to be close to the exact values of the effective properties of the composite. The numerically calculated values of the effective two-dimensional bulk and shear moduli of the composite are shown in Table 7.7. The percentage difference of the effective bulk modulus from the exact value is also shown in the table.

The effective shear moduli predicted by all the three methods are identical and equal to the exact value. In case of the effective bulk moduli, the RCM predictions are the most accurate followed by GMC and the finite element based calculations. The finite element based calculations overestimate the effective two-dimensional bulk modulus by...
Table 7.6. Phase properties used for testing Hill’s equation and the exact effective moduli of the composite.

<table>
<thead>
<tr>
<th></th>
<th>Vol. Frac.</th>
<th>$E$ ($\times 10^3$)</th>
<th>$\nu$</th>
<th>$G$ ($\times 10^3$)</th>
<th>$K$ ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disks</td>
<td>0.7</td>
<td>3.00</td>
<td>0.25</td>
<td>1.20</td>
<td>2.40</td>
</tr>
<tr>
<td>Binder</td>
<td>0.3</td>
<td>3.58</td>
<td>0.49</td>
<td>1.20</td>
<td>60.00</td>
</tr>
<tr>
<td>Composite</td>
<td>1.0</td>
<td>3.22</td>
<td>0.34</td>
<td>1.20</td>
<td>3.82</td>
</tr>
</tbody>
</table>

Table 7.7. Numerically computed effective properties for a square array of disks with equal component shear moduli.

<table>
<thead>
<tr>
<th></th>
<th>$K_{\text{eff}}$ ($\times 10^3$)</th>
<th>% Diff.</th>
<th>$\mu_{\text{eff}}^{(1)}$ ($\times 10^3$)</th>
<th>$\mu_{\text{eff}}^{(2)}$ ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEM</td>
<td>3.98</td>
<td>4.4</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>RCM</td>
<td>3.92</td>
<td>2.7</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>GMC</td>
<td>3.66</td>
<td>-4.2</td>
<td>1.20</td>
<td>1.20</td>
</tr>
</tbody>
</table>

around 4.4% while GMC underestimates the bulk modulus by around 4.2%. Since the error of estimation of all the three methods is small, it is suggested that all three methods are accurate for low contrasts in the shear modulus. However, Hill’s equation does not appear to be suitable for determining the best numerical method of the three.

7.8 Summary and conclusions

Predictions from the phase interchange identity for the shear modulus are closely approximated by the finite element approach (FEM), the recursive cell method (RCM) and the generalized method of cells (GMC) for checkerboard composites with low modulus contrast. For higher modulus contrasts, the FEM approximations of shear moduli are the most accurate. The RCM predictions overestimate the shear modulus while GMC underestimates the shear modulus. The exact relations for materials that are rigid in shear show that all three numerical techniques are inaccurate. The exact relation for this class of materials that is applicable to checkerboard materials shows that the FEM calculations are the most accurate while both RCM and GMC perform poorly in comparison. Though the predictions of the Cherkaev-Lurie-Milton theorem are quite accurately predicted by
all three numerical methods for high modulus contrast composites, the FEM results show the least error between the original and the translated effective properties while the RCM results show the largest error. The exact relation for isotropic composites with components that have the same bulk moduli also shows that the FEM predictions are the most accurate though they are somewhat higher than the exact values. However, no such distinction between the three methods can be made using Hill’s equation. These results agree with previous studies for high modulus contrast, high volume fraction polymer bonded explosives using FEM, GMC, and RCM. Thus, exact relations can be used to determine the accuracy of numerical methods prior to the application of these methods to the estimation of effective elastic properties of composites.
CHAPTER 8

CONCLUSIONS

The effective properties of polymer bonded explosives (PBXs) are difficult to predict because of the complexity of these materials, particularly the high particle volume fraction and the strong modulus contrast between particles and the binder. Analytical approximations have been found to predict inaccurate values of the effective elastic properties of PBXs. In addition, rigorous bounds have been found to be widely separated and thus of little use for elastic property determination. Two-dimensional finite element simulations of mock PBXs and PBX 9501 have shown that two-dimensional models can provide reasonable estimates of effective elastic properties at various temperatures and strain rates. However, the particle size distribution, mesh discretization, and stress-bridging affect the estimates considerably. Results from simulations of mock explosives show that debonding of the particles from the binder can affect the effective properties significantly, both in tension and in compression.

This investigation has shown that the generalized method of cells (GMC) cannot be applied to high modulus contrast and high volume fraction particulate composites because of its incomplete accounting of stress-bridging and computational inefficiency at high levels of discretization. Renormalization approaches, such as the recursive cell method (RCM), may be used to model stress-bridging effects and are more computationally efficient than either GMC or finite element analyses. However, the stiffness of PBX 9501 is shown to be overpredicted unless large blocks of subcells are renormalized. Exact relations for composite properties are shown to be an effective means of assessing the accuracy of numerical methods such as finite elements, GMC and RCM. Thus, these exact relations can be used to choose an appropriate method for the simulation of PBXs. The overall conclusion of this dissertation is that the accurate prediction of the
effective elastic properties of these materials requires the detailed simulation of actual microstructures using accurate numerical techniques.

8.1 Future work

An extension to this study would be to simulate detailed three-dimensional models of polymer bonded explosives with damage. Such studies, though computationally intensive, would provide a better estimate of the accuracy of calculations in two dimensions. Other numerical techniques such as the integral equation methods, the Sinc method, and Fourier transform methods can be explored to determine the best approach for studies in two and three dimensions.

Another useful area for future work would be the modeling of polymer bonded explosives using computed tomography images of the microstructure in three dimensions. Such images would not only be able to capture the detailed microstructure of the material, but also cracks and debonds. The simulation method could be a particle-in-cell type of method such as the material point method, which is easily parallelized. The binder can be modeled more accurately as a viscoelastic material. These simulations could then be used to determine the macroscopic constitutive relations for polymer bonded explosives.

However, the goal of multiscale modeling is not truly achieved if the microstructure to be simulated must be determined from experimental observations and measurements. Another avenue for future work would be to simulate the manufacturing process so that a realistic microstructure is generated computationally that can then be simulated.
APPENDIX A

TWO- AND THREE-DIMENSIONAL MODULI

The determination of the effective properties of random particulate composites using numerical techniques requires the use of a three-dimensional representative volume element (RVE). If a two-dimensional RVE is selected, any plane strain representation immediately implies that the material is composed of unidirectional cylindrical particles. On the other hand, if a plane stress representation is used, the physical interpretation of the composite is a thin sheet cut from the particulate composite.

One of the intents of this work has been to show that acceptable estimates of the effective elastic moduli of particulate composites can be obtained from two-dimensional plane strain calculations of the stress and strain fields. However, two-dimensional calculations in a single plane of the composite lead to two-dimensional or planar effective elastic moduli. For example, let a uniaxial uniform displacement $u_1$ be applied to a unit square of an isotropic, homogeneous, linear elastic material with Young’s modulus $E$ and Poisson’s ratio $\nu$ in plane strain. The resulting reaction force is $F_1$ and the displacement perpendicular to the direction of the applied displacement is $-u_2$. Since the square is of unit size, the nonzero strains are $\epsilon_{11} = u_1$ and $\epsilon_{22} = -u_2$. The nonzero stresses are $\sigma_{11} = F_1$ and $\sigma_{33} = \nu F_1$, the latter obtained from the constitutive relation

$$\epsilon_{ij} = (1/E)[(1 + \nu)\sigma_{ij} - \nu \sigma_{kk}\delta_{ij}] \quad i, j, k = 1, 2, 3.$$  \hspace{1cm} (A.1)

Note that $E$ and $\nu$ are three-dimensional or true linear elastic moduli. It can be shown that the apparent Poisson’s ratio in the plane ($\epsilon_{22}/\epsilon_{11}$) is given by

$$\nu_{2D} = \epsilon_{22}/\epsilon_{11} = u_2/u_1 = \nu/(1 - \nu)$$  \hspace{1cm} (A.2)

and the apparent Young’s modulus in the plane ($\sigma_{11}/\epsilon_{11}$) is given by

$$E_{2D} = \sigma_{11}/\epsilon_{11} = F_1/u_1 = E/(1 - \nu^2)$$  \hspace{1cm} (A.3)
These plane moduli, $E_{2D}$ and $\nu_{2D}$, are referred to as two-dimensional moduli following Jun and Jasiuk [31] and Torquato [84]. The reason for such a name is that these apparent moduli are the same as those obtained if the constitutive equations are expressed, in two-dimensional form, as

$$\epsilon_{ij} = \frac{1}{E_{2D}}[(1 + \nu_{2D})\sigma_{ij} - \nu_{2D}\sigma_{kk}\delta_{ij}] \quad i, j, k = 1, 2. \quad (A.4)$$

Finite element calculations shown in Chapters 3 and 4 suggest that these relations between two- and three-dimensional elastic moduli (which are exact only for isotropic, homogeneous, linear elastic materials) can be used to obtain reasonable approximations of three-dimensional elastic moduli of random particulate composites from two-dimensional numerical simulations.
APPENDIX B

ELEMENT STIFFNESS MATRICES

Explicit expressions for the stiffness matrix for four- and nine-noded displacement based elements and a hybrid nine-noded displacement/pressure based element (for nearly incompressible behavior) are discussed in this section. The explicit forms of the stiffness matrices eliminate the need for numerical integrations in the recursive cell method calculations. Schematics of the four- and nine-noded elements are shown in Figures B.1(a) and B.1(b).

B.1 Displacement-based four-noded element

The element stiffness of the four-noded displacement-based element is shown in Table B.1. Nodes 1 through 4 of the element are ordered in a counter-clockwise manner. There is no dependence of the stiffness matrix on element size or location.

B.2 Displacement-based nine-noded element

The element stiffness matrix for the nine-noded displacement based element in Figure B.1(b) is shown in Table B.2. This element can be used in conjunction with the nine-noded displacement/pressure based hybrid element. An orthotropic linear elastic material has been used to determine the element stiffness matrix. The stiffness matrix is, like that of the four noded element, independent of the location and size of the element.

B.3 Mixed nine-noded element

The binder used in PBXs is nearly incompressible and has a Poisson’s ratio of about 0.49. The volumetric strain in the binder is therefore small under applied loads. In displacement based finite elements, the element strain is determined from derivatives of displacements that are less accurately determined than nodal displacements. Therefore,
Figure B.1. Elements using in recursive cell method calculations. (a) Four-noded element (b) Nine-noded element.

Table B.1. Stiffness matrix for the displacement based four-noded element.

<table>
<thead>
<tr>
<th>2α</th>
<th>β</th>
<th>E</th>
<th>B</th>
<th>−α</th>
<th>−β</th>
<th>D</th>
<th>−B</th>
</tr>
</thead>
<tbody>
<tr>
<td>2γ</td>
<td>−B</td>
<td>F</td>
<td>−β</td>
<td>−γ</td>
<td>B</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>2α</td>
<td>−β</td>
<td>D</td>
<td>B</td>
<td>−α</td>
<td>β</td>
<td></td>
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<tr>
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Symm.

| 2γ  | −B  | F   |
| 2α  | −β  |
| 2γ  |

\[
\begin{align*}
\alpha &= \frac{1}{4}(C_{11} + C_{66}) , \\
\beta &= \frac{1}{4}(C_{12} + C_{66}) , \\
\gamma &= \frac{1}{4}(C_{22} + C_{66}) , \\
B &= \frac{1}{6}(C_{12} - C_{66}) , \\
D &= \frac{1}{6}(C_{11} - 2C_{66}) , \\
E &= \frac{1}{6}(C_{56} - 2C_{11}) , \\
F &= \frac{1}{6}(C_{22} - 2C_{66}) , \\
G &= \frac{1}{6}(C_{66} - 2C_{22}) .
\end{align*}
\]
Table B.2. Stiffness matrix for the displacement based nine-noded element.

| $j_2$ | $j_5$ | $e_2$   | $-j_5$ | $-j_6$ | $-j_8$ | $-j_9$ | $-j_1$ | $-j_2$ | $-j_3$ | $-j_4$ | $-j_6$ | $-j_7$ | $-j_1$ | $-j_2$ | $-j_3$ | $-j_4$ | $-j_5$ | $-h_2$ | $-h_3$ | $-h_4$ | $-h_5$ |
|------|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| $e_3$ | $-e_4$ | $j_6$   | $-f_2$  | $b_2$  | $d_1$  | $j_4$  | $d_3$  | $j_4$  | $f_1$  | $-b_2$ | $-a_1$ | $-b_1$ | $-j_1$ | $-j_2$ | $-j_3$ | $-j_4$ | $-a_1$ | $-b_1$ | $-c_1$ | $-b_1$ |
| $j_8$ | $j_5$   | $-h_4$  | $-j_3$  | $-i_1$ | $j_4$  | $g_3$  | $j_4$  | $g_1$  | $b_2$  | $-i_2$ | $-b_1$ | $-e_1$ | $j_5$  | $-e_4$ | $-j_6$ | $-i_1$ | $j_4$  | $g_3$  | $b_2$  | $-i_2$ | $b_1$  |
| $j_9$ | $j_5$   | $e_2$   | $-j_6$  | $d_3$  | $j_4$  | $f_1$  | $-b_2$ | $-f_2$ | $b_2$  | $d_1$  | $j_4$  | $-a_1$ | $-b_1$ | $j_8$  | $j_6$  | $j_3$  | $j_8$  | $j_6$  | $j_3$  | $j_8$  | $j_6$  |
| $j_8$ | $j_6$   | $-h_4$  | $j_4$   | $g_1$  | $b_2$  | $-i_2$ | $-b_2$ | $i_1$  | $j_4$  | $g_3$  | $b_2$  | $-i_2$ | $b_1$  | $-c_1$ | $-j_2$ | $-j_3$ | $-j_4$ | $-b_1$ | $-c_1$ | $-b_1$ | $-c_1$ |
| $j_9$ | $j_4$   | $g_1$   | $-j_4$  | $g_3$  | $b_2$  | $i_1$  | $-b_2$ | $-i_2$ | $b_1$  | $-c_1$ | $0$    | $-a_1$ | $b_2$  | $a_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  |
| $j_8$ | $j_6$   | $j_3$   | $-j_4$  | $d_1$  | $-j_4$ | $-f_2$ | $-b_2$ | $f_1$  | $b_2$  | $a_1$  | $0$    | $-c_1$ | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  | $-d_4$ | $0$    |
| $j_9$ | $j_4$   | $g_3$   | $b_2$   | $i_1$  | $-b_2$ | $-i_2$ | $b_1$  | $-c_1$ | $0$    | $-d_4$ | $0$    | $-a_1$ | $b_1$  | $a_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  |
| $j_8$ | $j_6$   | $j_3$   | $-j_4$  | $d_1$  | $-j_4$ | $-f_2$ | $-b_2$ | $f_1$  | $b_2$  | $a_1$  | $0$    | $-c_1$ | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  | $-d_4$ | $0$    |
| $j_9$ | $j_4$   | $g_3$   | $b_2$   | $i_1$  | $-b_2$ | $-i_2$ | $b_1$  | $-c_1$ | $0$    | $-d_4$ | $0$    | $-a_1$ | $b_1$  | $a_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  |
| $j_8$ | $j_6$   | $j_3$   | $-j_4$  | $d_1$  | $-j_4$ | $-f_2$ | $-b_2$ | $f_1$  | $b_2$  | $a_1$  | $0$    | $-c_1$ | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  | $-d_4$ | $0$    |
| $j_9$ | $j_4$   | $g_3$   | $b_2$   | $i_1$  | $-b_2$ | $-i_2$ | $b_1$  | $-c_1$ | $0$    | $-d_4$ | $0$    | $-a_1$ | $b_1$  | $a_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  |

Symmetry

| $e_3$ | $0$    | $-a_1$ | $-b_1$ | $-a_2$ | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    | $-a_1$ | $b_1$  | $d_2$  | $0$    |

| $h_3$ | $b_1$  | $-c_1$ | $0$    | $-c_2$ | $0$    | $g_2$  | $h_1$  | $0$    | $g_2$  | $16a_1$ | $0$    | $16a_1$ | $0$    |

| $a_1 = \frac{8}{45}(C_{11} + C_{66})$ | $a_2 = \frac{8}{45}(C_{11} - C_{66})$ | $b_1 = \frac{4}{3}(C_{12} + C_{66})$ | $b_2 = \frac{1}{3}(C_{12} - C_{66})$ | $e_3 = \frac{8}{45}(7C_{11} + 4C_{66})$ | $e_4 = \frac{1}{30}(7C_{11} - 4C_{66})$ | $f_1 = \frac{1}{30}(7C_{11} + 16C_{66})$ | $f_2 = \frac{1}{30}(7C_{11} - 16C_{66})$ | $g_2 = \frac{1}{15}(C_{22} + 4C_{66})$ | $g_3 = \frac{1}{15}(C_{22} - 4C_{66})$ | $h_1 = \frac{4}{45}(7C_{22} - 4C_{66})$ | $i_1 = \frac{1}{15}(7C_{22} + 16C_{66})$ | $i_2 = \frac{1}{15}(16C_{22} - 7C_{66})$ | $j_1 = \frac{1}{15}$ | $j_2 = \frac{7}{12}$ | $j_3 = \frac{1}{15}$ | $j_4 = \frac{1}{15}$ | $j_5 = \frac{8}{15}$ | $j_6 = \frac{1}{4}$ | $j_7 = \frac{1}{15}$ | $j_8 = \frac{7}{12}$ | $j_9 = \frac{1}{4}$ |
errors in the predicted volumetric strain for nearly incompressible materials can lead to large errors in the predicted stresses. Since the external loads are balanced by the stresses, this also implies that the predicted displacements will be inaccurate unless an extremely fine mesh is used. In practice, the displacements predicted by displacement based finite elements for nearly incompressible materials are much smaller than those expected [87]. This behavior is called element locking. The nine noded displacement/pressure element with three pressure degrees of freedom (also called a 9/3 u-p element) has been proven to avoid element locking [87]. This element is used for the RCM calculations on subcells containing the binder material. The 9/3 u-p element has the same geometry and node numbering scheme as that of the nine noded element shown in Figure B.1(b). The stiffness matrix for this element is shown in Table B.3 and is independent of size and location.
Table B.3. Stiffness matrix for nine noded mixed displacement/pressure element.

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$s y m m e t r y$

\(A = \frac{4}{3\pi} E/((1-2\nu)(1+\nu)), \quad a = 1-2\nu,\)

\(k_1 = 15 + \frac{137a}{4}, \quad k_2 = \frac{25}{4} + \frac{15a}{4}, \quad k_3 = \frac{15}{2} + \frac{5a}{4}, \quad k_4 = \frac{45}{16} + 10a,\)

\(k_5 = \frac{75}{8} - \frac{23a}{4}, \quad k_6 = \frac{135}{16} + \frac{15a}{4}, \quad k_7 = \frac{15}{8} + 4a, \quad k_8 = \frac{15}{2} - \frac{11a}{4},\)

\(k_9 = \frac{135}{4} - \frac{135a}{2}, \quad k_{10} = \frac{45}{4} + \frac{15a}{2}, \quad k_{11} = \frac{15}{2} + \frac{55a}{4}, \quad k_{12} = \frac{15}{4} - \frac{55a}{4},\)

\(k_{13} = \frac{45}{4} + 60a, \quad k_{14} = 30 - 32a, \quad k_{15} = 15 + 217a, \quad k_{16} = 15 - 11a,\)

\(k_{17} = 60 - 116a, \quad k_{18} = 105 + 205a, \quad k_{19} = 15 + 6a, \quad k_{20} = 120 - 116a,\)

\(k_{21} = 240 + 592a, \quad k_{22} = 15a, \quad k_{23} = \frac{45}{2}.\)
APPENDIX C

BOUNDARY CONDITIONS

The boundary conditions used to homogenize a block of subcells in RCM are a uniform normal displacement in the \(x\) direction (‘1’ direction), a uniform normal displacement in the \(y\) direction (‘2’ direction), and a shear displacement in the \(xy\)-plane (‘12’ plane). The goal is to simulate unidirectional normal stress states and pure shear stress states so that the effective properties of a block of cells can be calculated from the effective stress-strain equations.

The finite element problem involves the solution of a set of \(n\) linear equations relating the displacements \(u_j\) to the applied forces \(f_i\). This system of equations can be written as

\[
\sum_{j=1}^{n} K_{ij} u_j = f_i \quad (1 \leq i \leq n). \tag{C.1}
\]

The stiffness matrix is singular, and the set of equations can only be solved upon the application of suitable boundary conditions. The boundary conditions applicable for a block of four subcells are discussed below. Similar boundary conditions can be applied to a block of more than four subcells.

C.1 Normal displacement

A schematic of a block of four subcells subjected to a normal displacement in the \(x\) direction is shown in Figure C.1. The figure shows the locations of the nodes in the original and deformed configurations. A uniform displacement \(\delta\) is applied to nodes 3, 6, 9 and node 1 is kept fixed. Nodes 2 and 3 are not allowed to move in the \(y\) direction. Similarly, nodes 4 and 7 are not allowed to move in the \(x\) direction. To maintain perodicty of displacements, nodes 7, 8 and 9 are constrained to move an equal amount in the \(y\) direction. The pair of nodes 2 and 8 are constrained so that they move an equal amount in the \(x\) direction while nodes 4 and 6 are constrained so that they
Figure C.1. Schematic of the effect of a uniform displacement applied in the $x$ direction.

move an equal amount in the $y$ direction. The applied displacement $\delta$ and the fixed displacements at nodes 1, 2, 3, 4 and 7 are called the prescribed displacements. The constrained displacements are described by constraint equations. In equation form, the prescribed displacements used in Figure C.1 are

$$
\begin{align*}
    u_1 &= 0, & v_1 &= 0, & v_2 &= 0, & u_3 &= \delta, \\
    v_3 &= 0, & u_4 &= 0, & u_6 &= \delta, & u_7 &= 0, \\
    u_9 &= \delta, 
\end{align*}
$$

and the constraint equations for this case are

$$
\begin{align*}
    u_8 - u_2 &= 0, & v_6 - v_4 &= 0, & v_8 - v_7 &= 0, & v_9 - v_7 &= 0, 
\end{align*}
$$

where $u$ and $v$ are the nodal displacements in the $x$ and $y$ directions respectively and the subscript denotes the node number.

Similar boundary conditions apply when a uniform displacement is applied in the $y$ direction. The constraint equations are used to satisfy periodicity of displacements and may lead to stress states that are not purely unidirectional. However, for the materials under consideration, the deviations of the stresses from a unidirectional state of stress are small under the applied displacements.
C.2 Shear displacement

The simulation of a state of pure shear is more problematic. Two schemes have been examined for this process and are shown in Figures C.2(a) and C.2(b).

The scheme shown in Figure C.2(a) involves prescribing displacements that correspond to a pure shear at all the boundary nodes. In this approach, node 1 is fixed and node 9 is assigned displacements of magnitude $\delta_1 + \delta_2$ in the $x$ and $y$ directions. Node 3 is assigned a displacement $\delta_1$ in the $x$ direction and a displacement $\delta_2$ in the $y$ direction. Similarly, node 7 has prescribed displacements of $\delta_2$ in the $x$ direction and $\delta_1$ in the $y$ direction. The nodes on the boundary that are between the corner nodes are assigned displacements such that the boundaries remain straight lines. The values of $\delta_1$ and $\delta_2$

![Diagram](image)

**Figure C.2.** Displacement boundary conditions corresponding to a pure shear. (a) Prescribed displacements are applied at all the boundary nodes. (b) Prescribed displacements are applied only at corner nodes.
are chosen so that they correspond to a pure shear displacement. Application of such boundary conditions leads to relatively high normal stresses in the $x$ and $y$ directions and a relatively stiff shear response.

An alternative to this approach of application of shear displacement boundary conditions is shown in Figure C.2(b). In this case, the displacements are prescribed only at the corner nodes while the other nodes on the boundary are constrained so that they maintain periodicity. Thus node 8 is displaced relative to node 2 in the $x$ and $y$ directions by amounts corresponding to the shear displacement. A similar constraint equation relates the displacements at nodes 4 and 6. The normal stresses generated using this type of shear displacement boundary condition are much smaller than with the previous approach. However, when 9/3 u-p elements are used, unrealistic displacements may be obtained at node 5 which do not occur when the first approach is used.

The prescribed shear displacements for the approach shown in Figure C.2(b) are

\[
\begin{align*}
    u_1 &= 0, & v_1 &= 0, & u_3 &= \delta_1, & v_3 &= \delta_2, \\
    u_7 &= \delta_2, & v_7 &= \delta_1, & u_9 &= \delta_1 + \delta_2, & v_9 &= \delta_1 + \delta_2.
\end{align*}
\]

and the corresponding constraint equations are

\[
\begin{align*}
    u_6 - u_4 &= \delta_1, & v_6 - v_4 &= \delta_2, & u_8 - u_2 &= \delta_2, & v_8 - v_2 &= \delta_1.
\end{align*}
\]

### C.3 Application of constraint equations

The application of constraining relations follows the approach used in ANSYS 6.0 [86]. An equation that relates the displacements of two nodes is called a constraint equation. For example, for the case shown in Figure C.1 a constraint equation is

\[
    u_2 - u_8 = 0
\]

where $u_2$ is the displacement in the $x$ direction at node 2 and $u_8$ is the displacement in the $x$ direction at node 8. In this case, $u_2$ is the prime degree of freedom since it has a coefficient of $+1$. There can be many such constraint equations. In general form, these constraint equations can be written as,

\[
    \sum_{j=1}^{n} c_j u_j = C \quad (C.2)
\]
where $C$ is a constant. If $u_p$ is the prime degree of freedom then $c_p = 1$. For the recursive cell method calculations, the condition $c_p = 1$ is always satisfied.

Using the Lagrange multiplier technique, the original set of equations can be reduced by one to get a set of equations of the form:

$$\sum_{j=1}^{n} (K_{ij} - c_j K_{ip} - c_i K_{pj} + c_i c_j K_{pp}) u_j = f_i - CK_{ip} - c_i f_p + C c_i K_{pp} \quad (j \neq p) \quad \text{(C.3)}$$

Repeated application of this approach for each of the constraint equations gives us a set of equations with the redundant degrees of freedom removed. If there are $n_c$ constraint equations, the reduced system of equations can be written as

$$\sum_{j=1}^{n-n_c} K_{ij} u_j = f_i \quad (1 \leq i \leq n - n_c) \quad \text{(C.4)}$$

The specified displacements are used to further reduce the number of equations in the system shown in equation (C.4) in the usual manner before solving for the unknown displacements. At this stage, there are still some unknown nodal forces in the expressions for the force vector. These can be set to zero if we assume that the average forces are zero.

For the four subcell block subjected to a uniform normal displacement in the $x$ direction (shown in Figure C.1), these nodal forces are

$$f_{x_2} + f_{x_8} = 0, \quad f_{y_4} + f_{y_6} = 0, \quad f_{x_5} = 0,$$
$$f_{y_5} = 0, \quad f_{y_7} + f_{y_8} + f_{y_9} = 0.$$

where $f_x$ and $f_y$ are the nodal forces in the $x$ and $y$ directions, respectively. The subscripts 2, 4, 5, 6, 7, 8, and 9 refer to nodes at which the forces are applied. Similar equations are used when a uniform displacement is applied in the $y$ direction. For displacements that correspond to a pure shear (shown in Figure C.2(b)), we again assume that the constrained nodal forces average to zero. Therefore,

$$f_{x_2} + f_{x_8} = 0, \quad f_{y_2} + f_{y_8} = 0, \quad f_{x_4} + f_{x_6} = 0, \quad f_{y_4} + f_{y_6} = 0,$$
$$f_{x_5} = 0, \quad f_{y_5} = 0.$$

Once the unknown forces have been accounted for using the above procedure, the system of equations can be solved for the unknown displacements.
APPENDIX D

EFFECTIVE PROPERTIES

The effective stiffness matrix of a block of subcells can be obtained from equation (6.2) which relates the effective stiffness matrix to the volume averaged stresses and strains of the block. Since the subcells in a block are all the same size, the volume averaged stress or strain in a block is equal to the ensemble average of the average stresses or strains in each element.

For the four-noded element shown in Figure B.1(a), from the strain-displacement relations and integrating over the element, the volume averaged strains in the element are given by

\[
\langle \epsilon_{xx} \rangle = \frac{1}{2h} \left( -u_1 + u_2 + u_3 - u_4 \right),
\]

\[
\langle \epsilon_{yy} \rangle = \frac{1}{2h} \left( -v_1 - v_2 + v_3 + v_4 \right),
\]

\[
\langle \epsilon_{xy} \rangle = \frac{1}{2h} \left( -u_1 - u_2 + u_3 + u_4 - v_1 + v_2 + v_3 - v_4 \right).
\]

where \( u_i, v_i \) are the displacements at node ‘i’ in the \( x \) and \( y \) directions, respectively.

The average stresses can be obtained by plugging in the expressions for strain into the stress-strain relations and using the components of the stiffness tensor of the material in the element \( (C_{11}, C_{12}, C_{22} \text{ and } C_{66}) \). Similar expressions for the average stresses and strains can be obtained for the nine noded elements. For a RVE composed of many such elements, an arithmetic mean of the element average stresses and strains can be taken to calculate the volume average over the RVE.

The effective properties are related to the volume average stresses and strains by the relation shown in equation (6.2). For the case where a normal displacement is applied in the \( x \) direction, we have
\[ s^1_x = C^\text{eff}_{11} e^1_x + C^\text{eff}_{12} e^1_y \quad \text{(D.4)} \]
\[ s^1_y = C^\text{eff}_{12} e^1_x + C^\text{eff}_{22} e^1_y \quad \text{(D.5)} \]
\[ s^1_{xy} = C^\text{eff}_{66} e^1_{xy} \quad \text{(D.6)} \]

where \( s_x = \langle \sigma_{xx} \rangle, s_y = \langle \sigma_{yy} \rangle, s_{xy} = \langle \tau_{xy} \rangle, e_x = \langle \epsilon_{xx} \rangle, e_y = \langle \epsilon_{yy} \rangle, \) and \( e_{xy} = \langle \gamma_{xy} \rangle \). The superscript 1 represents normal loads in the \( x \) direction. When a displacement is applied in the \( y \) direction, we have

\[ s^2_x = C^\text{eff}_{11} e^2_x + C^\text{eff}_{12} e^2_y \quad \text{(D.7)} \]
\[ s^2_y = C^\text{eff}_{12} e^2_x + C^\text{eff}_{22} e^2_y \quad \text{(D.8)} \]
\[ s^2_{xy} = C^\text{eff}_{66} e^2_{xy} \quad \text{(D.9)} \]

where the superscript 2 represents normal loading in the \( y \) direction. For displacements in the \( xy \)-plane, we have,

\[ s^3_x = C^\text{eff}_{11} e^3_x + C^\text{eff}_{12} e^3_y \quad \text{(D.10)} \]
\[ s^3_y = C^\text{eff}_{12} e^3_x + C^\text{eff}_{22} e^3_y \quad \text{(D.11)} \]
\[ s^3_{xy} = C^\text{eff}_{66} e^3_{xy} \quad \text{(D.12)} \]

where the superscript 3 represents a shear load in the \( xy \) plane.

The equations (D.6) and (D.9) usually have very small values of stress and strain (close to zero) and are not used for the calculation of the shear stiffness term \( C^\text{eff}_{66} \). In some situations, the normal stresses in equations (D.10) and (D.11) are quite large compared to the shear stress in equation (D.12). However, the shear strain in equation (D.12) is much larger than the shear strains in equations (D.10) and (D.11). These two normal stress relations, D.10 and D.11, are ignored in the calculation of effective elastic properties. The effective stiffness matrix is easily calculated from the remaining equations (D.4), (D.5), (D.7), (D.8), and (D.12).
REFERENCES


