DISORDER-DRIVEN PRETRANSITIONAL TWEED MICROSTRUCTURES IN MARTENSITIC TRANSFORMATIONS

by

Sivan Kartha
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A Dissertation
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by
Sivan Kartha
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Defying the traditionally accepted understanding of first-order transitions, *solid-solid displacive transformations* are often accompanied by pronounced pretransitional phenomena indicative of a mesoscopic lattice deformation that "anticipates" the upcoming phase transition. Among these precurcive effects is the observation of the so-called "tweed" pattern arising in transmission electron microscopy in a wide variety of materials. We have investigated the tweed deformation in a two dimensional model system, and found that it arises because the compositional disorder intrinsic to any alloy conspires with the natural geometric constraints of the lattice to produce a frustrated, glassy phase. Within a Landau-Ginzburg framework, we develop a formalism which incorporates non-linearity and disorder. Analytically, we derive a formal, rigorous, mathematical mapping between this tweed system and an antiferromagnetic bipartite Sherrington-Kirkpatrick spin glass; a mapping which is exact in the limit of infinite elastic anisotropy. Even in real materials characterized by finite anisotropy, a glassy regime will still be present, as witnessed by hysteretic and frequency dependent experimental observations. We have employed numerical simulations to verify the predicted phase diagram and glassy behavior, and to produce diffraction patterns for comparison to experimental data. Analytically comparing to alternative models of strain-disorder coupling, we show that the present model best accounts for experimental observations.
BIOGRAPHICAL SKETCH

Born the third of Gopinath and Indira Kartha’s four sons, Sivan Kartha had the supportive and not overbearing encouragement of his parents in his early attempts to educate himself in the mysteries of science. Equipped with a second-hand chemistry set, and unencumbered by the stifling influence of text books or other sources of information, Sivan conducted experiments which generated chemical slurries of impressive toxicity. Timely intervention by his mother kept him from fulfilling his early aspiration of being responsible for his very own Superfund site, and encouraged him to seek out more innocuous fields of research.

His education continued at a series of schools known for their high-spirited frisbee teams, and before he knew it, he had a Ph.D. However, plagued by sudden guilt arising from the undeniable cushiness of his life on an otherwise trying planet, Sivan determined to commit himself to the common good (...as he sees it), shifting to the field of “policy physics.” Despite his utter lack of training, he hopes over the next few years to establish some credibility in the field, familiarizing himself with the problems and trying to figure out what exactly policy physics is.

Despite the long years he has invested in understanding tweed, Sivan is still suspicious regarding the comfort and practicality of garments stitched from the stuff, and has thus far delayed the purchase of a tweed jacket. This may not last, however, as contact with members of the policy field may inevitably drive him to discard the threadbare T-shirts and elbow-patched sweaters which currently typify his wardrobe.
എന്തെങ്കിലും സംഭവങ്ങൾ മാത്രമേ കാണാം എന്നും മനോരമമായ രാത്രിയെ എന്തെങ്കിലും പ്രായോഗികമായി നടത്തേണ്ട അന്തരി മലയാളം പ്രബലമായി കാണാം.
ACKNOWLEDGEMENTS

An incomplete and wholly unscientific investigation has provided evidence for what I have long suspected: the single word which appears in the thesis of every single advisee of Jim Sethna is the word enthusiasm, found in the acknowledgements, describing the advisor. Manifested in his indefatigable exuberance, his undying curiosity, and his energy even in the face of seemingly insurmountable barriers, Jim's enthusiasm has inspired the progress ("Progress ??") of those students who have been fortunate enough to study under him. No exception, I too, eventually did contract that contagious enthusiasm I once found manic, that optimism I had diagnosed as surely pathological. I truly thank him for passing on much more than simply knowledge, and for doing it with the patience and concern of a good friend.

The second unscientific investigation I've not yet finished, but I am convinced nonetheless: Jim Krumhansl's years of research, advising, and cooking have all derived their success from a common underlying philosophy: the flavor principle. An unfailing intuition allows Jim to sniff out the essence of problems, while his seasoned perspective directs him inevitably toward a well-balanced, organic whole, always colorfully garnished in his cheerful and humorous style. I thank him dearly for never really retiring.

My other Special Committee members, Bobby Pohl and David Mermin, I would also like to thank. More so than most A-exams, I believe, theirs was a source of inspiration and motivation, guaranteeing my continued academic progress. I further thank David Mermin, whose writing style reminds us that not all academic writing need be colorless and tedious.
For his encouragement and advice when I was baffled by career decisions, I would like to thank Kurt Gottfried, who indeed has long been an inspiring role model for physicists hoping to apply their training toward solving global problems.

For the computer services which made the computational aspects of my thesis possible, I thank the Materials Science Center of Cornell University, and for the financial support which made the final three years of my graduate career possible, I thank the U.S. Department of Education.

In the dead of the night while this dissertation was being furiously composed, I have often felt profound gratitude toward the anonymous author of the utility XCD. This magical little bit of code brought me the inspirational tunes of Billy Bragg, Seal, Bonnie Raitt and the Neville Brothers while I typed on and on.

Numerous officemates deserve thanks for their forbearance (and sometimes complicity) over the years, the most recent being Ernie Chan, Lisa Wickham, and Mark Oxborrow.

Not only has Douglas Milton honored my usually unreasonable pleas for help, (FedEx packages at 4:29pm, etc.) but he’s done so always with humor and never grudgingly. I certainly owe him much more than an IAS sweatshirt.

I happily thank Teresa Castán, who was involved in the early stages of this research, for teaching me that collaboration is not only productive, but it’s fun, sometimes even recreational.

Colleagues and fellow travelers Bruce Roberts and Karin Dahmen have helped me to maintain a healthy and good natured perspective toward graduate life. Bruce’s wry humor never ceases to find the comic in the tragic, and
Karin’s unending supply of smiles makes one doubt whether anything tragic exists anyway.

Thankfully, Christos Likos and Tom MacFarland have been largely unable to prevent me from distracting them from their research responsibilities, luring them into long and unresolvable debates on every imaginable topic, sometimes even physics. My education over the last five years owes much to their insight and thoughtfulness, and I am deeply thankful that our resulting friendships guarantee that those conversations will continue, (...by email when need be.)

Doctorate notwithstanding, the greatest part of my growth and learning while living here in Ithaca has come from outside the physics department, and this I owe to the friends with whom I have shared homes. Especially treasured among these friends are Jim Harkness, Nick Huntington, and Becky Williams, without whom I would have laughed much, much less, and Susan Ericsson, whom I simply thank fate for leading into my life.

These five years in Ithaca have allowed me to be at the geographic center of my somewhat spread out family. I received this gift without realizing how valuable it was, nor how much I would appreciate it over these years. I’ve been able to be with my family much more than would have been possible had I been elsewhere, and I am dearly grateful that this has made me aware of a closeness that is far more than merely geographical.
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Chapter 1

Martensitic Transformations

"While materials science has much in common with condensed matter science, an important difference is that it must include a science of 'dirt' if we are to have any hope of understanding the phenomena governing the behavior of the technologically important subset of condensed matter that we call materials."

G.B.Olson, K.Tsuzaki, and M.Cohen

Introduction

This important difference is quickly disappearing. A science of "dirt" has been developing within condensed matter physics, under the respectable yet sterile name of "disordered systems." This thesis is an attempt to demonstrate that condensed matter physics may, after all, have something to contribute to those materials science questions that are complicated by disorder, muddied by dirt, and everywhere present.

The practical relevance, the intriguing technical questions, and the sheer ubiquity of phase transitions have guaranteed their study a central role in not only condensed matter physics, but the natural sciences in general. However, unlike the extensive studies of phase transitions in magnetic, superfluid, and liquid systems where second-order transitions accompanied by critical phenomena have been studied for their formal challenge, we deal here with the solid-solid transformations which are overwhelmingly common in materials science. We are considering systems in which the lattice deforms from one crystalline phase to another through large-scale motions that preserve the topological integrity of the lattice. Commonly, these motions can proceed at sonic speeds, quite unlike diffusive or order-disorder transformations requiring the interchange of atoms.

The complexity of this type of transformation, in terms of the processes by
which they occur and the varied structures which they involve, has lead to the present study of the pretransitional phenomena and mesostructure of so-called martensitic transformation.

The underlying reasons why materials undergo martensitic transformation are as diverse as the materials in which they occur, and it would take us too far afield to discuss them in detail here\(^3\). Rather, in this thesis research we are concerned with how Landau-Ginzburg free energy functions, expressed in terms of quasi-static lattice distortive order parameters can be used to treat martensitic mesostructures and pretransitional phenomena. Within that philosophy it is assumed that from experiment, or eventually from theoretical considerations, a microscopic underpinning for the Landau-Ginzburg methodology can be developed. This assumption is reasonable because we are concerned with first-order transitions where thermal critical fluctuations are inconsequential. A general introduction to this viewpoint has been given by Barsch and Krumhansl\(^4\). Here we begin by detailing the basic ideas relevant to martensitic transformations, and introducing some of the varied real-world examples of this type of transformation.

Martensitic Transformations: Background

The word “martensitic” is not familiar, generally, except among metallurgists. Its history is a fascinating story, worth telling briefly. One of the great periods of change in civilization occurred when steel replaced bronze. Yet, it was entirely unknown what gave steel its valuable properties, and for centuries the techniques for making high quality steel were closely held, almost alchemical, secrets. Clearly, iron was its major component, but a myriad of other minor additions were found empirically, and even more mysterious treatments
were evolved for cooling the red hot object to room temperature — unlikely manufacturing processes such as adding mixtures of blood, and aging times which depended on the phase of the moon, for example. In the 19th century there were great advances in chemical analysis, and metallurgists had faith that the reasons why steels were different would soon be known through determination of differences in chemical composition. However, these hopes were soon dashed, as it was often found that various steel alloys with very similar compositions could have vastly dissimilar mechanical properties. Chemistry not having provided the answer to the steel puzzle, the answer was to come eventually from a distinctly different area of science — optics. There were great strides in optics over the same period, particularly in Germany, and in c. 1890, a gifted German microscopist Adolf Martens examined the microstructure, and found, not visible to the naked eye, many varieties of patterns at the micron scale. In particular, hard steels were found to have banded regions of differently oriented, fascinating microcrystalline phases, whereas inferior steels had little coherent patterning. The characteristic patterned regions became known as “martensite,” after their discoverer. The realization that the microscopic patterning might be just as important as composition in determining a material’s properties was a watershed in metallurgy; and a whole new subfield, “metallography” was born. Since that time hundreds of materials with martensitic morphology have been discovered and studied. To give just one sample of the richness of patterning in these many martensite, we show in Figure 1.1 patterns observed in at three different scales, 100, 1, and .01 microns, the last image unresolvable until the advent of electron microscopy. The patterning in Figure 1.1a and Figure 1.1b has been studied for nearly a century now and is extensively documented. However, the “tweed”
pattern, Figure 1.1c, is another matter, and it will be the main focus of this thesis.

Martensitic transformations are solid-solid phase transformations occurring between two different crystalline structures. By definition, these transformations are not reconstructive, that is, bonds between neighbors are not broken and re-formed; there is no diffusion and atoms maintain their relationship with their neighbors. Rather, these transformations are displacive, meaning there is some homogeneous strain that transforms one lattice into the other, with atoms moving in a cooperative fashion. A simple example is the transformation of a square lattice into a rectangular lattice, brought about by stretching along one axis and shrinking along the other. Such transformations have sometimes been termed “military” transformations, in order to convey the impression of a large-scale coordinated motion of an entire lattice, proceeding in lock-step from one configuration to another. This is in contrast to the relative anarchy of, say, a diffusive transformation, in which the atoms wander in search of a locally favorable environment, i.e. molecules in a vapor diffusing to find a home on a droplet.

Among solid-solid displacive phase changes generally, martensitic transformations are distinguished by the fact that the homogeneous strain which transforms one lattice into the other is dominated by shear displacements, so there tends to be relatively little volume change; on the order of no more than a few percent. Volume changes of this magnitude can be considered small especially in view of the fact that in certain non-metallic systems, the abrupt changes in volume associated with some first-order transition can be extreme enough to cause the crystal to shatter. Still, martensitic transformations are first-order transformations, and there can be substantial disruption occurring in the lat-
Figure 1.1  Microstructure seen in martensitic materials on three distinct length scales. a) Martensitic plates arranged in an austenite matrix. b) Twinned bands in a martensitic plate. 3) Tweed texture in transmission electron micrograph.
tice, such that in some materials the transformation will generate an audible "popping" as it propagates through a sample.

Aside from a homogeneous shear, which can be thought of as a static \( q = \frac{2\pi}{\lambda} = 0 \) phonon, some martensitic transformations include also a \( q \neq 0 \) component. If commensurate with the lattice, this modulation can be seen as a "shuffling" of atoms within a new unit (super-)cell. This is an appropriate description, for example, of a lattice that transforms to a close-packed structure with some long-period stacking sequence. (Materials which develop a periodicity of as many as eighteen lattice constants are known.) Certain solid-solid structural transformations, such as the \( \omega \)-phase seen in the Group IV elements, are \( q \neq 0 \) deformations, but include no homogeneous strain, and are technically not considered martensitic transformations.

This homogeneous strain and its symmetry-related variants are responsible for the experimentally observed characteristic (often elevated to the status of a defining characteristic) of martensitic transformations that they result in a "strain-controlled morphology." Indeed, the complex morphology found in the martensitic phase consists of a rather dazzling assortment of possible domain arrangements\(^6\): visually stunning and rather intriguing structures such as twinned lamellae, "herring bone," wedges of precisely determined proportions, and fine branching at interfaces. Further, the interaction of these domains and the response of this mesostructure to external forces and changes in temperature underly the "shape memory" phenomena that has brought such widespread attention to that class of martensitic materials. Hence, the challenge to understand the exact cause of these structures is one of the forces currently guiding research in martensitic transformations.
The strain-controlled morphology of martensitic structures results from the change in shape that a homogeneous strain produces. If a single crystal is slowly and carefully transformed from the high temperature phase to the martensitic phase by the gradual motion of a single interface that sweeps across the entire volume of the sample, (for example, if the experimentalist sets up a controlled temperature gradient) then, admittedly, the resulting microstructure will not be a complex multi-domain structure, but may simply be a single crystal of a new lattice structure and new macroscopic shape (perhaps, with a regular array of twins). Outside of these highly idealized circumstances, however, localized regions in real-world samples will transform under the constraints of the surrounding matrix. When a region of the sample changes shape, the resulting misfit will strain the surrounding lattice, generating misfit-induced long range elastic strain fields that will influence the subsequent transformation behavior. It is the subtle interaction of long range strain fields, and the need to minimize the total strain energy, that generates the complex and fascinating mesostructure which is universally observed in martensitic materials.

Classes of Martensitic Materials

Although the group of metals, alloys, and compounds known as martensitic materials exhibit a wide range of properties and behaviors, it is possible to very generally divide these materials into the following three categories without too severely obscuring their true diversity. The first class is the strongly first-order materials, primarily ferrous steels. It was in these materials that the martensitic transformation was first observed by metallographer Adolph Martens in the nineteenth century. The martensitic transformation in these materials involves a relatively large volume change, typically ~5%, and thus generates not
only large elastic strain fields but also substantial plastic accommodation at the (fcc)martensite-(bcc)austenite interface. For example, the dimensions of a disc-shaped martensitic plate of thickness \( t \) and radius \( r \) embedded in the parent matrix will be determined by minimizing the following sum of free energy contributions\(^{10}\):

\[
\Delta F = -\pi r^2 t \Delta f + 2\pi r^2 \sigma + \pi r^2 (A + B) \tag{1.1}
\]

where the “chemical” free energy difference between the two phases \( \Delta f \) is the available driving force; the interfacial energy \( \sigma \) includes plastic deformation energy, and the final term scales with the plate volume and includes an elastic component \( A \) and a plastic component \( B \). A large undercooling is needed to initiate the transformation, as a large free energy driving force is necessary to counterbalance the substantial energy which goes into the elastic and plastic deformation in the lattice. The martensitic transformation starts at some temperature, denoted \( M_S \), and continues with further cooling until some final temperature, \( M_F \), when the entire sample has transformed. Transformation in these alloys tends to occur athermally: it occurs during cooling, but is arrested when temperature is held constant; thermal equilibration does not play a significant role. The martensite forms via a “burst” mechanism, that is, as plates are formed they immediately grow to their full size with a speed comparable to the speed of sound. Similarly, heating the sample causes the reverse transformation, starting at \( A_S \) and ending at \( A_F \), with a very substantial degree of hysteresis, e.g. \( A_S - M_S \approx 400^\circ K \) in FeNi.

The second class of martensites is the moderately first-order materials. The volume change is relatively small, typically \( \lesssim 1\% \), and there is little plastic deformation of the lattice needed to accommodate the developing martensite
(e.g. AuCd, NiTi, NiAl, FePD, CuZnAl, each over a range over alloy concentrations.) As a result, the hysteresis is substantially smaller in these materials than in the strongly first-order martensites, and the undercooling produces correspondingly less excess free energy, which is entirely stored recoverably in the elastic strain fields. In such cases, the martensitic transformation is called thermoelastic, i.e. there is a quasi-static equilibrium maintained between the "thermal" bulk free energy driving the transition and the elastic strain fields created in the material,

$$\Delta F = -\pi r^2 t \Delta f + \pi rt^2 A.$$  \hspace{1cm} (1.2)

The transformation is then fully reversible: as the temperature is reduced and the driving force increases, the transformed region grows until it is balanced by the increased elastic energy. If the temperature is then raised again, the transformed region shrinks until the elastic energy once again balances the bulk free energy. A relatively insignificant amount of energy is expended in plastic deformation, and the temperature hysteresis in this case is only a few degrees rather than hundreds of degrees.

Interestingly, the reversible nature of the thermoelastic martensitic transformation apparently requires not only that the transformation strain be small enough to render plastic deformation unnecessary, but also that the alloy have an ordered structure. Because of the parent lattice's crystallographic symmetry, it can transform to one of a number of symmetry related martensite lattices, called martensite variants. Similarly, the reverse transformation can return to one of a number of symmetrically related parent lattices. Although this degeneracy of possible return transformations exists crystallographically, in ordered crystals the original structure is the only one which also preserves the original ordering. Convincing experimental evidence of this argument is provided
by FePt, which is thermoelastic if ordered, but non-thermoelastic when disordered! Further, the only thermoelastic alloys which are not ordered are those which undergo a FCC→FCT transition, which, for sufficiently small strain, is crystallographically reversible even when disordered.

It is this reversible nature of the thermoelastic martensitic transformation which leads to the shape memory effect. Figure 1.2 is an example of an idealized two dimensional material which undergoes a martensitic transformation from a square crystalline phase to a rectangular one. Clearly, the martensitic phase has two variants (long and skinny, short and wide) and below the transformation temperature the sample will be composed of a multi-variant structure of the martensitic phase, in this case a twinned structure which approximately preserves the overall square shape of the sample. Straining this sample will cause domains of one variant to grow at the expense of the other, and the sample appear to plastically deform to a new shape which better accommodates the applied strain. Unloading the sample leaves it deformed, but upon heating above the transformation temperature, the sample snaps (with surprising force!) back to the original macroscopic shape. This is the basic phenomena underlying the shape memory effect, whose substantial practical and industrial use is just now starting to be tapped.

The third class of materials are the nearly second-order martensites, e.g. the superconducting A-15's (V₃Si and Nb₃Sn), the Indium-rich alloys (InTl and InCd). The transformation in these cases has an extremely small discon-
Figure 1.2 The high temperature square phase transforms to a twinned microstructure of the two low temperature variants. Applying an external strain induces apparent plastic deformation, which spontaneously reverses upon heating back above the transformation temperature. This is the shape memory effect.
tinuity, typically $\sim 0.1\%$, hysteresis of only a few degrees, $(3 - 4^\circ K)$, and a thermoelastic transformation. These materials share the distinctive trait that they all show drastic elastic or phonon softening as the transformation temperature is approached from above, that is, the harmonic response to a particular mode radically decreases in frequency (and energy).

It is clear that these martensitic materials defy the traditional theoretical understanding of first-order transformations. The physicist's idealized first-order behavior consists of an abrupt transition point with little interesting accompanying phenomena. In contrast, the complex hysteresis behavior and pretransitional phenomena exhibited in martensitic transformations have long intrigued metallurgists and the materials scientists. Among these phenomena is the distinctive pretransitional lattice modulation known as "tweed." Enlisting the aid of tools and perspectives from the field of condensed matter physics, this research aims to disentangle the general physical principles from the confusing and often distracting material specific details of this widely observed phenomena. In doing so, we hope to contribute to the effort to unravel tweed.

The structure of the remainder of this thesis is as follows: chapter 2 is an overview of some of the major ideas which have been developed to explain the transformation mechanism in martensites. Chapter 3 introduces the topic of pretransitional phenomena and specifically tweed, and the discusses the role of compositional disorder. Chapter 4 presents our methods for studying the problems of mesoscale structure and the pretransitional phenomena for which it is responsible. Chapter 5 uncovers a "spin-glass" phase corresponding to the tweed regime in the limit of infinite elastic anisotropy. Chapter 6 relaxes the anisotropy condition, and analyzes tweed as it appears in a real system via numerical simulation. Chapter 7 analyzes the tweed deformation generated by
this model and compares it to experimental observation. Chapter 8 shows that the long-range strain interactions can be expressed as a non-local interaction in the order parameter, effectively renormalizing the Fourier space elastic constants. Chapter 9 considers alternative mechanisms for coupling the disorder to strain, and discusses their effectiveness at generating tweed. Chapter 10 offers a general conclusion, briefly mentions additional research already explored, and suggests avenues for experimental investigation. Appendix A discusses in detail the construction of the Landau free energy. Appendix B gives a simple argument for tweed correlation length scales based on balancing energies. Appendix C supplies the required black and white versions of color pictures included in earlier chapters.
First order transformations, by their very definition, occur between phases which are in some significant way quantitatively different. For example, a drop of water has a density which differs substantially from the vapor in which it may sit. The finite jump of the order parameter across a phase boundary is generally not a comfortable occurrence for a system, and it will tend to fight such discontinuities. Thus arises the tricky question of what nonequilibrium process causes such phase transitions to actually occur in systems in which they should in principle occur. How does the system proceed from one phase to the other, and how does it tolerate the unpleasant intermediate step when the two phases are juxtaposed?

This very standard problem is typically treated using “nucleation theory” or “critical droplet theory”\textsuperscript{12}—a straightforward balancing of surface and volume energies. The problem is rather more daunting in the case of solid–solid transformations, so we shall for the moment adopt the language of a liquid–vapor transition. Suppose a volume of vapor has been cooled to just below the transition temperature. If a small spherical droplet were to transform in this otherwise untransformed system, it would incur a free energy cost due to the boundary between the droplet and the vapor environment; the liquid’s surface tension results in a surface energy, $F_s = (4\pi r^2)\sigma/r$ (where $r$ is the droplet radius, and $\sigma$ is the surface tension which creates a surface energy density $\sigma/r$.) On the other hand the bulk free energy is lower for the liquid phase, so there is a free energy gain, $F_b = -(\frac{3}{2}\pi r^3)\Delta f$, where $\Delta f$ is the difference between the free energy densities of the two phases. The surface energy scales like $r$, whereas
the change in bulk energy scales with the size of the transformed droplet, \( r^3 \), so, extremizing the total energy with respect to \( r \), we find a critical droplet size, \( r^* = \sqrt{\sigma/\Delta f} \), with free energy \( f^* = \frac{8}{3} \pi \sigma \sqrt{\sigma/\Delta f} \). Smaller droplets are unstable to shrinking, but larger droplets are unstable to growing. As random thermal motion jostles around the molecules in the system, subcritical droplets will be assembled, and just as quickly shrink away. The transformation will finally occur when one such droplet of the critical size actually forms, and grows to consume the entire system. The rate at which such thermal activation produces such a critical droplet is proportional to \( e^{-f^*/k_b T} \), so at temperatures small compared to \( f^*/k_b \), thermal activation will never occur on a reasonable time scale. This brings us to the question of whether martensitic transformations, (indeed, any first-order solid-solid transformations) are nucleated in this classical way: Is the energy barrier associated with the critical nucleus small enough for thermal activation to drive the transformation?

This question was one of the early pressing items of research in martensitic transformations, and fairly thorough reviews now exist\(^{13,14,15,16,17}\). The nucleation of martensite within an austenite matrix was early on analyzed in a manner analogous to the liquid–vapor case, with some significant modifications.\(^{18,19}\) First, the optimal morphology is generally not a simple sphere, but is more closely approximated by a thin plate with a radius \( r \) and a thickness \( c \), whose ratio is determined by the anisotropy of the lattice and the transformation strain. Typically, the surface energy of the nucleus is thus expressed \( F_s = (2\pi r^2)\gamma \). The surface energy density, \( \gamma \), is not easy to estimate, and will depend on the details of the phase boundary, that is, on what sort of violence has been done to the integrity of the lattice at the martensite–austenite interface. The naive picture of a perfectly coherent interface quickly gave way to a picture of a semi-
coherent interface in which an array of parallel dislocations is the price paid for accommodating the lattice mismatch between the austenite matrix and the martensite nucleus\textsuperscript{20}.

Second, there is an additional contribution to the energy due to the fact that the transformation is a shape-changing transformation, and the transformed particle no longer fits into the matrix of which it is part. There will be a strain field generated in the surrounding matrix as the lattice attempts to accommodate the deformed martensitic nucleus. This is a long range strain field and cannot simply be absorbed into the expression for surface energy, but rather must be integrated over the system. Still, extremizing the expression for the energy of an inclusion, taking into account the surface energy, the long range strain energy, and the bulk energy difference between the phases, we can get an expression for a critical $r^*$ and $c^*$. When such a calculation is done for a typical ferrous martensite\textsuperscript{19,20}, Fe-Ni\textsubscript{30}%, the resulting critical nucleus is fairly huge, $\sim$ 2 million atoms, and the free energy barrier is far from surmountable: $f^* = 3 \cdot 10^5 k_b T M$!

The above argument is based on early estimates of free energies which are likely to be quite imprecise. Currently, much more sophisticated total energy calculations are being done\textsuperscript{21} which can yield information about not just the bulk energy of the phases, but in principle also interfacial energies. Directly determining free energies from these $T = 0$ total energy calculations is still difficult, but much information regarding the vibrational contribution to entropy can be garnered from phonon dispersion curves.

Although the values for energies used in the arguments against thermal nucleation of martensite are in need of revising, it can still be argued that this type
of nucleation in a uniform system, or "homogeneous nucleation" is essentially impossible, and is not the operative mechanism. Clever experiments have been done which clearly demonstrate that martensitic nucleation is "heterogeneous," it relies on some nonuniformity in the system. Early experiments on small particles of FeNi30%\textsuperscript{22} and subsequent analyses\textsuperscript{23,24} revealed that the fraction of transformed particles increases with decreasing temperature in a way which is particle size dependent. This dependence implies a nucleation mechanism which relies on pre-existing nucleation sites in the lattice. A similar conclusion is implied by observations of small austenite precipitate (Fe) in a copper rich Cu-Fe sample\textsuperscript{25}. These precipitate particles did not transform at all, even well below the bulk transformation temperature for iron. However, when the Cu-Fe sample was deformed, driving defects into the precipitate particles, transformation was observed in the precipitate particles.

A substantial amount of work has been done trying to establish the nature of the nucleation sites. Early on, Kaufman and Cohen\textsuperscript{20} suggested the possibility of "embryos" of the low temperature phase which were frozen-in as a sample was quenched from high temperature. At sufficiently high temperatures, such excitations might conceivably be common, although they are of very high free energy and may well be unstable. Subsequent experiments on Fe-30%Ni by Korenko and Cohen\textsuperscript{26} have been interpreted as evidence that this nucleation mechanism cannot be important. Noting that the martensitic embryos in Fe-30%Ni would be ferromagnetic, they annealed under a high magnetic field. Although the field should increase the embryo density and size they found that there was no corresponding increase in the nucleation rate.

Fisher \textit{et al.}\textsuperscript{27} proposed that nucleation could occur on compositional inhomogeneities in the sample. For example, the free energy driving force and
transformation temperature both increase with decreasing carbon content in Fe-C, so regions with relatively low carbon content may be the regions to transform first. However, even assisted by a carbon-free area which is the size of a critical nucleus, the nucleation barrier is prohibitively large in Fe-C. The fundamental problem is, once again, the prohibitively large elastic strain and interfacial energy associated with a critical embryo existing in an otherwise untransformed matrix. The benefit of a driving force which is increased by carbon deficiency is simply not sufficient to overcome the costly constraints of coherency with the surrounding lattice and elastic strain throughout the lattice. However, the role of compositional variation will be taken up in greater detail later, specifically with regard to phenomena more subtle than the wholesale transformation of a macroscopic sample of material.

The nucleation mechanisms which have received most attention have been those mechanisms which rely on lattice defects and pre-existing strain fields. Early on, Cohen, Machlin, and Paranje\textsuperscript{28} advanced the theory that strain fields within the lattice could distort local regions toward the martensitic configuration, and that these regions would serve as “strain embryos.” As temperature was decreased below some threshold, these strain embryos would become unstable toward growth into the martensitic phase. Elaborating on this idea, Olson and Cohen\textsuperscript{29} considered how a pre-existing array of dislocations can convert into a martensitic nucleus. Particular configurations of dislocation arrays were shown to be capable of dissociating into partial dislocations such that they bound a region which is martensitically deformed, and become a semi-coherent interface with the undeformed matrix. For a large enough array of dislocations, the array becomes unstable to growth at some temperature. For typical ferrous martensites undergoing a FCC→BCC or FCC→HCP transformation, the size
of the array is roughly four or five dislocations and are sufficiently common as to be a likely source of nucleating sites. For BCC→ closed-packed lattices (such as FCC and 9R) typical of the thermoelastic martensites, the array size is substantially larger, and the scarcity of such defects may make this mechanism unimportant\textsuperscript{13}.

Another set of theories have considered the possibility that elastic anharmonicity will assist defects in bringing about the martensitic transformation. Since the transformation is occurring at a temperature where the parent structure is metastable and the martensitic structure is stable, sufficiently large distortions from the parent structure will be affected by the existence of the metastable phase because anharmonic terms will become important. Indeed, a sufficiently deformed parent lattice will be mechanically unstable, or at least soft, to full transformation. This mechanism, termed the "localized soft mode", has been compared to spinodal decomposition. In spinodal decomposition, compositional fluctuations in a metastable system cause local excursions into the stable phase and facilitate the transformation, whereas, here, strain "fluctuations" due to defects drive the metastable lattice toward a "strain spinodal" beyond which the stable martensitic phase lies. A continuum elasticity analysis which takes into account third order elastic constants\textsuperscript{30,31} has determined which strain modes lead to mechanical instability most readily, and their relation to certain martensitic transformations. Calculations for certain materials (Li, Na, CuZnAl) find that strains of only a few percent are capable of bringing about the transformation.

The various theories described above seek to uncover the nature of the heterogeneous nucleation in martensitic transformations. However, it is useful to explain the homogeneous transformation mechanism which is thought
to be responsible in many second-order displacive structural transformations, and discuss its applicability to the nearly second order martensitic materials. In the many materials which are truly second-order, as well as in the nearly second-order martensites, there is typically a drastic elastic or phonon softening observed before the transformation which has been reasonably assumed to play an important role in the transformation itself. Significantly, the particular elastic modulus or phonon mode which softens in these cases is indeed the mode which measures the harmonic response of the lattice to exactly that distortion which deforms the parent lattice into the product lattice. For example, the A-15's\textsuperscript{32} and the Indium alloys\textsuperscript{33} undergo a cubic $\rightarrow$ tetragonal transformation which occurs by shearing of (11) planes, and there is indeed softening of the $C'$ elastic modulus, which measures the response of the lattice to (11) shears. Similarly, the second-order tetragonal $\rightarrow$ orthorhombic transformation in the 2-1-4 superconductors corresponds to an optical phonon which tips the oxygen octahedron around the copper atom\textsuperscript{34} and it is this phonon mode which is seen to soften. Also, the relevant mode in various second-order perovskite transitions also are seen to soften prior to the transition\textsuperscript{35}. Because of this recurring relationship between the softening elastic or phonon mode and the transformation deformation, it has frequently been argued that the transformation in these materials is a "soft mode transition." The soft mode transformation, as proposed initially by Cochran\textsuperscript{36} and by Anderson\textsuperscript{37}, arises from the softening of some mode all the way to $\omega = 0$, and the ensuing mechanical instability which drives the lattice into the martensitic deformation. This transformation would then be continuous and second order.

Applying a soft mode analysis to these materials is indeed tempting. For example, in the 2-1-4 materials and in the perovskite SrTiO\textsubscript{3}, there does appear
to be full softening of the relevant mode, and a corresponding second-order transition, which is not martensitic. The soft mode viewpoint in these cases seems to be appropriate, and it is possible to investigate the critical phenomena expected for a soft mode transition\(^{38}\) in these systems\(^{39}\).

On the other hand, for the A-15's and Indium alloys, although the softening is quite severe indeed, (in InTl the anisotropy grows to \(c'/c_{44} = 287\) at the transition!) the straightforward application of a soft mode analysis is not appropriate. On symmetry grounds alone, the cubic \(\rightarrow\) tetragonal transformation in these materials must be first order. It may intuitively seem possible for the transition to be second-order, because there is no obvious geometrical picture to explain why the \(c/a\) ratio cannot simply increase continuously from zero, (more formally, the tetragonal point group is a sub-group of the cubic point group). However, a proper symmetry analysis shows that this transition fails the Landau criterion (it has a cubic invariant of the order parameter) for a second-order transition. Reassuringly, these materials do in fact undergo a first-order transition, not a second-order transition as a true soft mode would imply. (For quite some time, before before \(V_3Si\) was finally identified as actually having a weakly first-order rather than second-order\(^{40}\) transition, it was widely touted as being the sole counter-example to the Landau criterion for a second-order transition!) Thus, a soft mode model is inapplicable here, as the following experimental evidence bears out: 1) Most importantly, the above materials indeed show an (admittedly small) discontinuity in the strain at the transformation; for \(V_3Si\) the change in unit cell volume is only a few parts per hundred thousand\(^{40}\). 2) The elastic softening is not complete, the modulus does not diminish all the way to zero. 3) There is some finite, if small, hysteresis. 4) Transformation requires nucleation. 5) There tend to be no critical fluctuations.
6) Far above the transition temperature, apparently stable "precursors" of the martensitic phase appear which cannot be accounted for by soft-mode theory. Explaining this would require a theory that would permit stable heterophase fluctuations, or the introduction of some heterogeneous mechanism, perhaps disorder. This matter is a central focus of this research.

While the ultimate mechanical instability of a lattice as envisioned in the "orthodox" soft mode theory does not take place in first order transitions, it does not follow that the softening mode should be disregarded and that a study of the phonons (by neutron scattering, raman scattering etc.) is irrelevant. In fact, the low lying modes will still be easily driven by applied stresses of the correct symmetry, and are the leading candidates for order parameters in Landau type formulations of displacive transformations \cite{41,42}.

It is clear from the above discussion that the problem of nucleation in martensitic materials is far from being fully settled; the process is surprisingly difficult to explain. This makes even more mysterious the existence of precursors, behavior which suggests that lattice is anticipating the transformation as much as 100°K above the transformation temperature! The next chapter will offer a brief description of pretransitional phenomena in various martensitic materials, and propose compositional disorder as their source.
Chapter 3
Pretransitional Phenomena, Tweed, and Compositional Disorder

Like the skyward gazing astronomer who can best perceive an obscure celestial object with a slightly averted view, the condensed matter physicist too has learned to turn away from the direct scrutiny of phase transitions per se, and instead to investigate their accompanying critical phenomena. The critical fluctuations which herald second order phase transitions have served as a rich source of experimental data, and have spurred the development of powerful and general theoretical constructs such as the renormalization group, critical scaling and universality. In contrast, no such diversity of curious pretransitional behavior exists in classic first order phase transitions: the water-ice transition is not heralded by critical fluctuations, length scales do not diverge, and there are no widespread anticipatory excursions into the approaching phase. Subsequently, systems undergoing first order phase transitions have been lost in the shadows of their glamorous second order cousins such as the superconducting, magnetic, and fluid transitions.

However, this unfair situation has arisen only because the classic models of first order transitions (such as the Ising model in an external field below its Curie temperature) have not done justice to real systems undergoing first order transitions. Materials scientists and metallurgists have long associated first order transitions with complex hysteresis behavior and pretransitional phenomena. In this chapter, we will discuss the nature of the pretransitional effects in martensitic materials, and their relation to the transformation. In particular, we will introduce the experimentally observed pretransitional phenomena which is the object of study of this thesis: tweed.
3.1 Pretransitional Phenomena in Martensites

Whereas critical phenomena in second order phase transitions are associated with thermally excited fluctuations in the order parameter near the transition, pretransitional phenomena in first order displacive structural phase transitions have a wide variety of manifestations, defying a single description or even a systematic categorization, and they occur even far above the transition, sometimes more than one hundred degrees (K) above. For the moderately and weakly first order martensites, pretransitional phenomena have virtually become the norm rather than the exception. Measurements have been made of precurvus anomalies in thermal expansion coefficients, acoustic attenuation, internal friction, electrical resistivity, and other transport coefficients. The most illuminating observations of pretransitional phenomena have been through scattering experiments using x-rays, neutrons, and electrons as probes. In x-ray experiments, "ghost" spots (both commensurate and incommensurate with the reciprocal lattice) and diffuse scattering (beyond the expected thermal diffuse scattering) have been observed. Neutron measurements have revealed marked pretransitional softening of entire phonon branches and of well defined phonons, as well as anomalous elastic (or, perhaps quasi-elastic?) scattering known as the "central peak." Transmission electron microscopy has uncovered anomalous scattering behavior like that found in x-ray scattering, allowing us to view the corresponding real space phenomena, both in conventional and (ultra-)high resolution.
3.2 Tweed

It is these TEM studies which have inspired this research, by intriguing us with the baffling nature of the pretransitional phenomena they revealed. Most impressive is the so-called tweed texture shown in Figure 3.1 which belies some spectacular large scale coordinated lattice modulation, in stark contrast to the expected monotony of a flat field pitted by the occasional defect. First seen by Lee Tanner in the mid-sixties in CuBe\textsuperscript{58}, it was named after the textile with the same characteristic pseudo-periodic cross-hatched diagonal pattern. Since that time, tweed has been observed in many materials undergoing structural phase transformations: shape memory alloys such as NiAl\textsuperscript{55,59}, FePd\textsuperscript{56,60,61}, FePt\textsuperscript{62}, CuZnAl\textsuperscript{63}; high temperature superconductor YBCO\textsuperscript{57,64,65}, and the A-15 superconductor V\textsubscript{3}Si\textsuperscript{66}; materials undergoing ordering transitions, spinodal decomposition and precipitation (NiAl, FePt, FePd, CuBe, and steels\textsuperscript{7}).

In some of these materials, the tweed appears as a transient state through which the sample passes during the early stages of a coarsening process, and it disappears with time or with additional tempering. (See Ref. 68 and references therein.) In these materials the tweed is well described as resulting from microdomains of precipitate within a solute matrix and their surrounding long-range strain fields. However, tweed is usually seen as an apparently unchanging state which is stable during aging or tempering. It appears reversibly and repeatedly upon heating and cooling through the phase transition, and is therefore assumed to be a stable, non-transient configuration. Tweed cannot be a metastable state in which the system is stuck as it attempts to globally transform from austenite to martensite, because the system chooses to return to the state as it is reheated. The questions with which this thesis is concerned
Figure 3.1 Tweed in as seen in the shape memory alloy Ni$_{67}$Al$_{23}$ in the austenite phase prior to its martensitic transformation.$^{67}$
are: 1) what is the precise nature of the tweed deformation? and 2) what is the driving force causing tweed to arise?

Tweed observations and their accompanying electron diffraction observations have uncovered certain important facts about the nature of the tweed deformation. It was immediately recognized that tweed is associated with diffraction patterns which are consistent with the presence of \{110\} planes shearing in (110) directions. This strain, the so-called Zener mode\(^{69}\) has a particular significance for many of the most common martensitic transformations. The square \(\rightarrow\) rectangular transformation, the cubic \(\rightarrow\) tetragonal transformation and the tetragonal \(\rightarrow\) orthorhombic transformation all result from precisely such \{110\}/(1\bar{1}0) shears. In addition, this shear (coupled with an additional homogeneous strain) is responsible for body-centered cubic \(\rightarrow\) close-packed transformations. The observation of a pretransitional deformation which involves this particular shear is therefore very consistent with the approach of the martensitic transformation. Furthermore, it is this shear mode that couples to the elastic constant \(C'\) which is seen to soften in many materials as the martensitic transformation temperature is approached. The precise nature of the shears has resisted quantitative analysis, with various studies suggesting static\(^{65}\) or dynamic\(^{70,71}\) waves\(^{66}\) or distinct martensite microdomains (or “embryos”) and their surrounding strain fields arising from point defects\(^{72}\), phonon anomalies\(^{73}\), entropy driven fluctuations\(^{74}\) or local atomic orderings\(^{59,57,75,68,76}\). The single fact agreed upon by all is that the deformation is composed predominantly of \{110\}/(1\bar{1}0) shears.

The relationship between the \{110\}/(1\bar{1}0) shear and the martensitic transformations strain is one example of the general observation that pretransitional phenomena often have a distinct connection to the ensuing phase transition:
the softening of the appropriate elastic constant or phonon, the appearance of diffraction intensity at martensite Bragg peaks, the central peak at $q$ vectors corresponding to the martensitic structure, for example. Pretransitional phenomena are considered pretransitional not only because they occur when a phase transition is anticipated, but also because they typically imply the presence of some lattice disturbance which is suggestive of the ensuing phase. This suggests that there may exist some highly effective yet very general mechanism by which the low temperature phase is making its presence felt even far into the high temperature phase.

### 3.3 Disorder and Pretransitional Phenomena

One very general and important experimental observation has attracted our attention to disorder as a candidate mechanism. Alloys undergoing martensitic transformations can be extremely sensitive to the relative alloying percentages of the elements which make them up. For example, Fe$_{1-x}$Pd$_x$ undergoes its martensitic transformation at room temperature when $\eta = 29\%$, but as $\eta$ is increased to 32%, the transformation temperature, $T_M$, plummets to absolute zero: a one percent shift in the concentration of palladium causes a drastic $100^\circ K$ drop in $T_M$! This is not at all atypical of alloys and doped compounds which are martensitic, rather a wide variety of materials show this same extreme sensitivity of transition temperature on composition or dopant concentration. Indeed, typical binary alloy phase diagrams$^{77}$ are simply abounding with phase boundaries at precipitous angles.

As discussed in the introductory chapter, the physical processes underlying the martensitic transformation vary from one material to the next. It is therefore impossible to generically ascribe this composition sensitivity to a single
physical mechanism. However, a convenient way to think of this drastic compositional sensitivity is to consider the martensitic transformation as a fixed temperature phase transition which occurs as composition $\eta$ is varied and passes through some critical composition. The drastic dependence of transformation temperature on composition can then be viewed as simply an extremely weak temperature dependence of the critical composition.

Why, then, should this weak temperature dependence of critical composition be so widespread a phenomena? Or, rephrased more precisely: Why is the energy scale associated with a small change in composition comparable to the energy scale associated with a large change in temperature? The answer must be material specific, but in general the energy scale of the relevant physical processes is typically in the $\sim 0.1 - 1\, \text{eV}$ range: Fermi energies, variations of band structure with atomic species, crystal structure energy differences, mixing energies of solid solutions, pair interaction energies, and species dependent chemical potentials are all on roughly on this energy scale, so a change of composition of $\sim 100\%$ would be on this energy scale as well. On the other hand, the range of temperature explored in the typical laboratory is a few hundred meager degrees, corresponding to a energy range of only $\sim 25\text{meV}$. A parameter such as the critical composition mentioned above should be expected to vary by a only a few percent ($\sim 25\text{meV}/1\text{eV}$) over a seemingly large temperature range. In some sense, the perceived drastic composition dependence is simply a reflection of our own anthropocentric view of reality. We are not terribly robust creatures, and are therefore limited to a fairly narrow temperature range while we explore the physical world. A few hundred degrees impresses us as a dramatic change in temperature, while an electron is impressed by nothing less than a Fermi temperature.
This composition dependence of the transformation temperature is a commonly observed property of many of the martensitic materials that show pre-transitional behavior. In our opinion, this property bears directly on the question of precursors and it offers some insight into their ubiquity. Since composition in any alloy or doped compound is a spatially inhomogeneous quantity, the actual composition will vary around some average composition simply due to the disorder that is frozen in as the solid forms from the melt. Since the transformation temperature is so sensitive to composition, there must exist a locally defined hypothetical transformation temperature which depends on the local composition. This local transformation temperature may be higher or lower than the observed transformation temperature, whereupon the first sign of bulk transformation is observed in a given sample and long range martensitic order is actually established. For example, a small region in a sample of FdPd which has a lower than average concentration of palladium will seek to transform into the martensitic phase well before the transformation temperature at which the bulk martensitic order finally develops. The static, quenched-in, purely statistical compositional disorder will determine the spatial variation of local transformation temperature, and it is this disorder which will lead to pretransitional deformations occurring on a mesoscopic scale in a otherwise untransformed lattice.

In actuality any local tendency to transform may be suppressed by the surroundings which may not be ready to transform. Therefore, the essence of this problem is to treat the overall system as a collection of local regions which interact via extended strain fields. It cannot be a simple superposition of different transformable units, and models which simply consider isolated defects may ignore important collective effects. The remainder of this thesis is
the development and investigation of a model for tweed, in which compositional disorder is the stimulus, and long-range cooperative behavior the response.
Chapter 4

A Mesoscale Model for Tweed

In this chapter, we seek to develop a model for a system which exhibits a tweed regime. The key physics incorporated into the model will be compositional disorder and its coupling to the martensitic transformation, as discussed in the previous chapter. We will view the material as an elastic continuum, and analyze it within a Landau-Ginzburg framework governing the lattice distortive free energy. Pursuing this approach, we construct a general free energy which is consistent with the symmetries of the system and which is taken to sufficiently high order in the relevant strain order parameters to produce the important physical behavior. The parameters in the resulting free energy are related to empirically measurable materials constants, such as elastic constants, phonon dispersion curves, couplings to impurities, lattice constants etc. In this chapter, the model will be introduced for two and three dimensional materials, but subsequent chapters will investigate the behavior of the model primarily in the two dimensional case.

The experimentally observed tweed pattern suggests the existence of some deformation superimposed on an otherwise intact lattice, having a lengthscale of several lattice constants, or several tens of lattice constants. Indeed, behavior on any length scale can ultimately be reckoned back to the quantum mechanics underlying the system on an atomic and electronic scale. However, tweed is seen in such a wide variety of systems, under such a wide variety of circumstances, that it is valuable to explore the tweed phenomena independent of the microscopic peculiarities of specific materials and independent of the precise atomic behavior which underlies a material. In order to exploit the generality of the
tweed phenomena, and to most effectively study a phenomena which occurs on a length scale somewhat greater than the lattice constant, we will adopt a perspective which focuses on this *mesoscale* structure, and leaves the atomistic behavior of the material largely unspecified.

The natural starting place is to consider the material simply as an elastic continuum. Traditionally, this perspective has been fruitful in studying homogeneous deformations in harmonic (Hooke's Law) materials; cleanly and effectively treating bodies of various geometries under conditions of stress or torsion, homogeneous or inhomogeneous\textsuperscript{85,86,87}. Extension of this approach to systems where anharmonicity is important has provided a tool for general treatment of more complicated problems, for example materials undergoing martensitic transitions\textsuperscript{4,41,88,89,90,91,92,93}. On the microscopic level, martensitic transitions involve the displacement of atoms from one crystalline lattice structure to another— an atomic scale rearrangement which might appear to have little to do with continuum elasticity. However, as explained in the introductory chapter, these microscopic motions occur via a homogeneous strain which takes place over a macroscopic region of the lattice, i.e., they are *displacive*, not *reconstructive*. The material thus behaves on mesoscopic length scales like an elastic continuum. Extending the traditional linear continuum elasticity approach by considering higher order strain terms is the natural way to include the physics underlying the shape-changing transformation.

This extension of continuum elasticity beyond harmonic order can be systematically carried out within the well established Landau–Ginzburg formalism\textsuperscript{88,94}. As always, an order parameter is defined which characterizes the nature of the phase transition under consideration, and group theory is em-
ployed to determine a general free energy functional which is consistent with the symmetries of the system and the order parameter.

In order to maintain a certain degree of generality, we choose a common, perhaps prototypical, system for our investigation: the two dimensional square to rectangular martensitic transformation, and its three dimensional analog the cubic to tetragonal martensitic transformation. In each of these transformations the unit cell distorts from the higher symmetry phase to the lower by stretching along one axis, (typically denoted the \( c \) axis,) and contracting along the other(s), (the \( a \) axis). (In some cases, the \( c \) axis contracts and the \( a \) axes expand, e.g. \( \text{Nb}_3\text{Sn} \).) Both of these martensitic transformations are very commonly observed in many technologically important materials. The square to rectangular transformation is realized in materials as the equivalent (from a symmetry perspective) tetragonal to orthorhombic transformation, which is seen in quasi-two dimensional planar materials such as the high temperature superconducting ceramics. Superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) and other materials based on the same structure, (the "1-2-3" superconductors), are observed to undergo such a martensitic transformation as temperature is lowered, and also as the oxygen concentration \( \delta \) or the concentration of a dopant (such as Fe, Al, or Co substituting for the Cu) is varied\(^{95,96} \). \( \text{La}_2\text{CuO}_4 \) and other materials based on the same structure, (the "2-1-4" superconductors), undergo a tetragonal to orthorhombic transformation\(^{97,98,89} \) as well, via a different mechanism.

The cubic to tetragonal transformation is exhibited in a variety of different materials: certain shape memory alloys such as \( \text{FePd}^{60,99} \), \( \text{FePt}^{62} \), \( \text{MnCu}^{100} \) and certain indium alloys\(^{101} \), for example, undergo a face-centered cubic \( \rightarrow \) face-centered tetragonal transformation. The superconducting A-15 compounds\(^{32} \), \( \text{V}_3\text{Si} \) and \( \text{Nb}_3\text{Sn} \), transform from cubic to tetragonal, as well.
The well known harmonic continuum theories for materials with square and cubic symmetries is our starting point. The general form of an elastic free energy is given by:

$$F = \frac{1}{2} \sum_{i,j,k,l} \lambda_{ijkl} e_{ij} e_{kl}$$

(4.1)

where the elastic modulus tensor $\lambda_{ijkl}$ satisfies the symmetries of the system and the $e_{ij}$ are components of the strain tensor $\mathbf{e}$, defined as the non-rotational part of the displacement gradients,

$$e_{ij} = \frac{1}{2} \left( \frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} + \frac{\partial U_i}{\partial x_i} \frac{\partial U_j}{\partial x_j} \right).$$

(4.2)

The second order term guarantees that finite rotations are not included in the strain tensor, but in general this term is very small for these applications, and we have safely neglected it in our analytical work, although all numerical simulations include it.

The general form (4.1), which has $2^4 = 16$ terms in two dimensions and $3^4 = 81$ terms in three dimensions is simplified when $F$ is required to be invariant under the symmetries of the material in question. The free energy for a material with square symmetry (point group $C_{4v}$) simplifies to

$$F = \frac{1}{2} \lambda_{xxxz}(e_{xx}^2 + e_{yy}^2) + \lambda_{xxyy} e_{xx} e_{yy}$$

$$+ 2\lambda_{xyxy} e_{xy}^2$$

(4.3)

while a three dimensional material with cubic symmetry (point group $O_h$) simplifies to

$$F = \frac{1}{2} \lambda_{xxxz}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \lambda_{xxyy}(e_{xx} e_{yy} + e_{yy} e_{zz} + e_{zz} e_{xx})$$

$$+ 2\lambda_{xyxy}(e_{xy}^2 + e_{yz}^2 + e_{zx}^2).$$

(4.4)
We rewrite each of the expressions for the free energy as follows. For the two dimensional case,

\[ F = \frac{A_\phi}{2} \phi^2 + \frac{A_1}{2} e_1^2 + \frac{A_2}{2} e_2^2 \] (4.5)

where the strains \( \phi, e_1, \) and \( e_2 \) are defined by

\[ \phi \equiv \frac{(e_{xx} - e_{yy})}{\sqrt{2}}, \quad e_1 \equiv \frac{(e_{xx} + e_{yy})}{\sqrt{2}}, \quad \text{and} \quad e_2 \equiv e_{xy} \] (4.6)

and their respective coefficients are related to the standard nomenclature by

\[ A_\phi \equiv \lambda_{xxxx} - \lambda_{xyyx} \equiv c_{11} - c_{12} \equiv 2C' \] (4.7a)

\[ A_1 \equiv \lambda_{xxxx} + \lambda_{xyyx} \equiv c_{11} + c_{12} \] (4.7b)

and

\[ A_2 \equiv 4\lambda_{xyxy} \equiv 4c_{44}. \] (4.7c)

For the three dimensional case,

\[ F = \frac{A_\phi}{2}(\phi_{xx}^2 + \phi_{yy}^2 + \phi_{zz}^2) + \frac{A_1}{2} e_1^2 + \frac{A_2}{2}(e_{xy}^2 + e_{yz}^2 + e_{zx}^2). \] (4.8)

Here, the redefined strains follow a pattern similar to the two dimensional case:

\[ e_1 \equiv (e_{xx} + e_{yy} + e_{zz})/\sqrt{3} \] (4.9a)

and

\[ \phi_i \equiv e_ii - \frac{1}{3} e_1. \] (4.9b)

and their respective coefficients are

\[ A_\phi \equiv \lambda_{xxxx} - \lambda_{xyyx} \equiv c_{11} - c_{12} \equiv 2C' \] (4.10a)

\[ A_1 \equiv (\lambda_{xxxx} + 2\lambda_{xyyx})/3 \equiv (c_{11} + 2c_{12})/3 \] (4.10b)
and

\[ A_2 \equiv 4\lambda_{xyz} \equiv 4c_{44}. \]  

(4.10c)

In (4.5) and (4.8), we have expressed the energy not in terms of the basic components of the strain tensor, \( e_{ij} \), but in terms of linear combinations which are easily interpreted geometrically. Conveniently, this new basis also has a clearer relationship with the square \( \rightarrow \) rectangular (cubic \( \rightarrow \) tetragonal) martensitic transformation strain. In both cases, the strain \( e_1 \) reflects a “bulk dilatational strain,” i.e. an expansion along each of the body axes. The strain \( e_2 \) in the two dimensional case, and the strains \( e_{xy}, e_{yz}, \) and \( e_{zz} \) in the three dimensional case, correspond to a diamond shaped deformation of the continuum, referred to as “diagonal strain” or “shear strain.” The strains which are of particular interest in this investigation are distinguished in both cases by the use of the greek character \( \phi \). These strains correspond directly to the martensitic transformations under study, and are referred to as “deviatoric strains.” A positive value of \( \phi \) reflects a rectangular shaped deformation, expanding along the \( x \)-axis and contracting along the \( y \)-axis. Similarly, in three dimensions, the strain \( \tilde{\phi}_x \) corresponds to an expansion along the \( x \)-axis and a contraction along the other two axes, i.e. a tetragonal deformation. The obvious analogous descriptions apply to \( \tilde{\phi}_y \) and \( \tilde{\phi}_z \). Note that in two (three) dimensions, \( \phi \) is defined to be a rectangular (tetragonal) deformation that leaves area (volume) unchanged, i.e. it is linearly independent from bulk dilatation.

The utility of this change of variables is evident. We have now reexpressed our free energy in terms of an order parameter, \( \phi \) in 2-d, and \( \tilde{\phi} \equiv (\tilde{\phi}_x, \tilde{\phi}_y, \tilde{\phi}_z) \) in 3-d) which locally describes the degree of martensitic transformation: it is zero in the austenite phase, and non-zero in the martensite phase. The devi-
atoric strain order parameter will play the central role in our analysis of the
tweed problem, and the other strains – bulk dilatation and diagonal strain –
will play the role of secondary degrees of freedom. The precedence of $\phi$ over
the other strains will be a central thread through the ensuing analysis. First,
our Landau–Ginzburg approach will adopt $\phi$ as its order parameter. Second,
Chapter 5 will introduce the approximation of infinite anisotropy, in which
only the deviatoric strain order parameter is taken to be important, and expli-
cate an analysis which maps the martensitic material onto a spin glass. Third,
Chapter 6 and Chapter 7 will return to the full elastic problem, (i.e., no approx-
imation of infinite anisotropy) and develop a numerical simulation and present
its results. The remaining 2 chapters then return to analytical investigation of
the unconstrained elastic problem, and reinterpret the secondary strain fields
as mediators of a long range interaction acting on the order parameter field.

The definition given above for the order parameter in three dimensions (the
deviatoric strain components $\tilde{\phi}_x$, $\tilde{\phi}_y$, and $\tilde{\phi}_z$) is useful for descriptive purposes,
but not the most appropriate choice for carrying out further analysis. The
reader may have observed that the deviatoric strain fields are not linearly in-
dependent, since $\sum_i \tilde{\phi}_i = 0$. The order parameter for the cubic $\rightarrow$ tet.ragonal
transition is actually just the two dimensional object which, along with $e_1$,
spans the same space as $e_{xx}$, $e_{yy}$, and $e_{zz}$. This does not uniquely define a pair
of strains, so we are free to choose according to personal preference. For future
convenience, we choose

$$
\phi_1 \equiv (-e_{xx} - e_{yy} + 2e_{zz})/\sqrt{6} \quad \text{and} \quad \phi_2 \equiv (e_{xx} - e_{yy})/\sqrt{2}
$$

The three dimensional harmonic free energy is then

$$
F = \frac{A_1}{2} (\phi_1^2 + \phi_2^2) + \frac{A_1}{2} e_1^2 + \frac{A_2}{2} (e_{xy}^2 + e_{yz}^2 + e_{xz}^2). \quad (4.12)
$$
and now
\[ A_\phi \equiv (\lambda_{zzz} - \lambda_{zyy})/2 \equiv (c_{11} - c_{12})/2 \equiv C'. \] (4.13)

Note that the new order parameter strains \( \phi_1 \) and \( \phi_2 \) couple to the same elastic constant as the previous strains, \( \phi_x, \phi_y, \) and \( \phi_z \). The three tetragonal martensitic deformations, (i.e. tetragonal deformations with the expansion along any one of the three axes,) are typically expressed in terms of the elastic strain tensor as:
\[ e = \epsilon \left( \begin{array}{ccc} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{array} \right) \text{ for } \hat{c} \parallel \hat{x} \] (4.14)

with the obvious modifications for \( \hat{c} \parallel \hat{y} \) and \( \hat{c} \parallel \hat{z} \). The standard crystallographic measurement of tetragonality is related to (4.14) by:
\[ \frac{c}{a} - 1 = \frac{1 + 2\epsilon}{1 - \epsilon} \approx 3\epsilon. \] (4.15)

Reexpressing in terms of the redefined order parameter \( \phi = (\phi_1, \phi_2) \), we have:
\[ \hat{c} \parallel \hat{x} : \quad \phi = \epsilon(-\sqrt{6}/2, 3\sqrt{2}/2) \] (4.16a)
\[ \hat{c} \parallel \hat{y} : \quad \phi = \epsilon(-\sqrt{6}/2, -3\sqrt{2}/2) \] (4.16b)
\[ \hat{c} \parallel \hat{z} : \quad \phi = \epsilon(\sqrt{6}, 0) \] (4.16c)

as the three tetragonal martensitic variants.

As is appropriate for any Landau approach, the next step is to expand the free energy in terms of the order parameter, \( \phi \). Please refer to Appendix A for details. We will start with the harmonic free energy as expressed in Eqs. (4.5) and (4.12) and extend to higher order in the order parameter, extending to the minimum order that is necessary to guarantee that we have included the important physics. In this case, this means that the free energy is taken
to sufficient order to produce a first order phase transition. It is important to note that, despite the first order nature of the phase transitions, expanding in the order parameter is indeed legitimate: the transformation strains in systems in which we are interested are small, typically a few percent at most.

For the two dimensional system, scalars with respect to the square symmetry group can be constructed from the order parameter simply by taking any even power of $\phi$. Subsequently, the minimum order in $\phi$ needed to insure a first order phase transition is sixth order, and the Landau free energy takes the form

$$ F = \frac{A_\phi}{2} \phi^2 - \frac{B_\phi}{4} \phi^4 + \frac{C_\phi}{6} \phi^6 + \frac{A_1}{2} e_1^2 + \frac{A_2}{2} e_2^2 $$

Here, for positive $B_\phi$ and $C_\phi$, a first order transition occurs as $A_\phi$ decreases through some (positive) critical value $A_\phi^{\text{crit}} = \frac{3B_\phi^2}{16C_\phi}$, as depicted in Figure 4.1. It is important to note, in light of the discussion in Chapter 2 regarding the application of soft mode theory to first order structural phase transformations, that the first order transition does not require full softening of the elastic constant $A_\phi$ all the way to zero. The second order transition can be modeled by considering only the second and fourth order terms above (i.e. a $\phi^4$ model), whereupon a soft mode transition will occur (for $B_\phi > 0$) as $A_\phi$ passes through zero.

For the three dimensional system, the higher order scalars which can be constructed from the two component order parameter $\phi$ yield a first order transition by taking terms only up to fourth order, and the resulting free energy takes the form
Figure 4.1 The free energy for the two dimensional system, shown as the quadratic coefficient is swept through the critical value.
Again, for positive $B_\phi$ and $C_\phi$, a first order transition occurs as $A_\phi$ decreases through some positive critical value $A_\phi^{\text{crit}} = 2B_\phi^2/9C_\phi$. As can be seen in Figure 4.2, between the inflection point at which martensitic phase first appears as a metastable phase ($A_\phi^{\text{meta}} = B_\phi^2/4C_\phi$) and the critical point at which the martensitic phase becomes the thermodynamically stable phase ($A_\phi^{\text{crit}} = 2B_\phi^2/9C_\phi$), very little softening of $A_\phi$ has occurred: the difference between the measured phonon frequencies (which go like $A_\phi^{1/2}$) will be less than 6%. This is pointed out in order to stress that this theory is distinct from the soft mode theory which has been applied with some success to a subset of second order structural phase transformations, and is meant to apply to the wider range of materials that undergo first order transformations, never exhibiting true soft mode behavior.

Note in particular that there exists a third order term, (in contrast to the two dimensional case), and the Landau criterion is therefore satisfied. This implies that a second order transition cannot occur for any system of cubic symmetry described by an order parameter with the same symmetry as $\phi$, and indeed, no second order transitions have been found in materials belonging to this class of systems. (See discussion in Chapter 2.) A second order transition would be seen in the parameter subspace in which $B_\phi$ is identically zero, however there is zero probability that a real material would fall in this subspace since a non-zero $B_\phi$ is symmetry-allowed. The nearly second order transitions that are seen in many materials arise from relatively small values of $B_\phi$. 

\[
F = \frac{A_\phi}{2}(\phi_1^2 + \phi_2^2) - \frac{B_\phi}{3}\phi_1(\phi_1^2 - 3\phi_2^2) + \frac{C_\phi}{4}(\phi_1^2 + \phi_2^2)^2
+ \frac{A_1}{2}e_1^2 + \frac{A_2}{2}(e_{xy}^2 + e_{yz}^2 + e_{zx}^2).
\] (4.18)
Figure 4.2 The free energy for the three dimensional system, shown as the quadratic coefficient is swept through the critical value. (The potential is shown inverted in order to more clearly display the minima.)
Eqs. (4.17) and (4.18) yield the "Landau" part of the Landau-Ginzburg free energy, i.e. the local terms but not the gradient terms. Recall, the tweed problem involves a nonuniform deformation, and spatial variation of the strain field is at the heart of the tweed mesostructure. Any investigation of this problem must include strain gradient terms, lest uncontrolled spatial variation be produced merely as an artifact of the incompleteness of the approach. For a thorough discussion of this issue see Ref. 102 and references therein. We thus consider scalars which can be constructed from the order parameter and the gradient operator \((\partial_x, \partial_y, (\partial_z))\), (see Appendix A) and find the appropriate Ginzburg terms to lowest order:

\[
F_G = \frac{\kappa}{2} (\nabla \phi)^2
\]

(4.19)
in two dimensions and

\[
F_G = \frac{\kappa_1}{2} (\partial_x (-\phi_1 + \sqrt{3} \phi_2))^2 + (\partial_y (-\phi_1 - \sqrt{3} \phi_2))^2 + (2 \partial_z \phi_1)^2 \\
+ \frac{\kappa_2}{2} (\partial_x (-\sqrt{3} \phi_1 + \phi_2))^2 + (\partial_y (-\sqrt{3} \phi_1 - \phi_2))^2 + (2 \partial_z \phi_1)^2
\]

(4.20)
in three dimensions.

The one piece of important physics which remains to be incorporated into this mesoscale model for tweed is the compositional disorder which has been described and motivated in Chapter 3. We would like to introduce a spatially varying composition field into the model, in such a way that it influences the martensitic transition temperature. Up to this point, we have simply stated that the martensitic transition occurs as the harmonic parameter \(A_\phi\) passes through some critical value\(^\dagger\), there being an assumed temperature dependence to \(A_\phi\).

\(^\dagger\) As discussed in Chapter 2, the transformation temperature observed in the laboratory will be below the thermodynamic critical temperature. Real samples build up long range strains, and therefore undercooling is needed in order to generate sufficient driving force to overcome strain energy.
The natural way to incorporate composition dependence into the transition temperature is to make this parameter depend explicitly on local composition as well as temperature. For simplicity, we shall consider a linear dependence, so

\[ A_\phi = A_\phi(T, \eta(x)) = A_T t + A_\eta \delta \eta(x) \]  

(4.21)

where the local composition inhomogeneity \( \delta \eta(x) \equiv \eta(x) - \bar{\eta} \) is defined relative to the average composition, and the temperature \( t = T - T_0(\bar{\eta}) \) is defined relative to the temperature at which the austenite becomes mechanically unstable in a sample of average composition \( \bar{\eta} \).

The compositional disorder we are considering is simply a scalar field which describes the relative concentration of a particular species. The simplest terms allowed by Landau's symmetry considerations which couple a scalar field and the order parameter are

\[ \eta \phi^2 \quad \text{and} \quad \eta (\phi_1^2 + \phi_2^2) \]  

(4.22)

in two and three dimensions, respectively, and these terms are implied by the expression (4.21). It must be emphasized that we are considering disordered alloys or doped compounds in which the positional disorder is simply substitutional. All lattice sites and only lattice sites are occupied, although their occupation is disordered with respect to atomic species. We are not considering interstitials or other defects which may have a non-trivial symmetry which allows them to couple to the order parameter through terms other than Eqs (4.22). Specifically, the point of this study is to proceed beyond the linear elasticity analysis which follows from a linear coupling to the order parameter, \( \eta \phi \), which is not allowed by symmetry for this model. (This point will be discussed extensively in Chapter 9.)
In summary, in this chapter we have extended the standard harmonic continuum elasticity model in order to apply it to materials undergoing a square $\rightarrow$ rectangular transition (two dimensions) or a cubic $\rightarrow$ tetragonal transition (three dimensions), introducing compositional inhomogeneities as a driving force for a spatially varying deformation. The free energy is assembled from the local terms, (Eqs. (4.17) and (4.18)), the gradient terms, (Eqs. (4.19) and (4.20)), and the coupling term, (Eq. (4.21)), yielding the final forms

$$F = (A_{TT}t + A_\eta \delta \eta(x))\phi^2 - \frac{B_{\phi}}{4} \phi^4 + \frac{C_{\phi}}{2} \phi^6$$

$$+ \frac{A_1}{2} e_1^2 + \frac{A_2}{2} e_2^2$$

$$+ \frac{\kappa}{2} (\nabla \phi)^2$$

in two dimensions, and

$$F = [A_{TT}t + A_\eta \delta \eta(x)](\phi_1^2 + \phi_2^2) - \frac{B_{\phi}}{3} \phi_1(\phi_1^2 - 3\phi_2^2) + \frac{C_{\phi}}{4}(\phi_1^2 + \phi_2^2)^2$$

$$+ \frac{A_1}{2} e_1^2 + \frac{A_2}{2} (e_{xy}^2 + e_{yz}^2 + e_{zx}^2)$$

$$+ \frac{\kappa_1}{2} \left( (\partial_x(-\phi_1 + \sqrt{3}\phi_2))^2 + (\partial_y(-\phi_1 - \sqrt{3}\phi_2))^2 + (2 \partial_z\phi_1)^2 \right)$$

$$+ \frac{\kappa_2}{2} \left( (\partial_x(\sqrt{3}\phi_1 + \phi_2))^2 + (\partial_y(\sqrt{3}\phi_1 - \phi_2))^2 + (2 \partial_z\phi_1)^2 \right)$$

in three dimensions.

Having established the above expressions for free energy functionals which govern the equilibrium behavior of the materials, we shall now turn to an analysis of that behavior.
Chapter 5

The Infinite Anisotropy Limit and the Spin Glass Model

In this chapter, we introduce an approximation which allows us to develop a rigorous, formal mapping from tweed to a spin glass. The approximation we introduce is, in essence, the approximation that the order parameter field, \( \phi \) is the only degree of freedom in this system. That is, we consider solutions of the model consisting of deformations consisting of \( \phi \) strain only, and no bulk dilation or diagonal strain. First, we relate this approximation to the materials science behavior which it reflects. We next show that elastic constraints resulting from this approximation do in fact permit a class of solutions, and we give the general form for these constrained solutions and compare them to the experimentally observed tweed deformation. We then show that within this class of constrained solutions, there is a formal mapping between the tweed model and a particular type of spin glass. This result casts an entirely new light on the nature of tweed and its relationship to the crystalline phases.

As introduced in the previous chapter, the elastic free energy functional depends on all components of the (irrotational) strain tensor, but \( \phi \) was singled out for special consideration because \( \phi \) is the order parameter for the structural phase transformations under consideration; it measures the degree of martensitic strain. The approximation being considered in this chapter, that \( \phi \) is the only non-zero component of the strain tensor, is equivalent to the approximation that the coefficients of the other strain components in the free energy are taken to be positive infinite, i.e. there is an infinite cost associated with the other strain modes. This is therefore an approximation of infinite anisotropy: the ratios between the elastic constant \( C' \) coupling to \( \phi \) strain and the elastic
constants $A_1$ and $A_2$ coupling to bulk dilation and diagonal strain ($(C_{11} + C_{12})$ and $4C_{44}$ in two dimensions, and $(C_{11} + 2C_{12})/3$ and $4C_{44}$ in three dimensions) are taken to be infinite.

In many materials, this infinite anisotropy approximation is quite a reasonable approximation. As discussed in Chapter 3, pronounced softening of the elastic constant $C'$ is often observed as a pretransitional effect, not only in materials undergoing the martensitic transformations we are considering here, but also other materials such as cubic to close-packed martensites, which also frequently display tweed. The degree of anisotropy varies markedly among materials, and in some materials (e.g. Indium compounds) the infinite anisotropy approximation can be assumed to be extremely valid, while for others, (e.g. YBCO) the approximation is suspect.

5.1 Constrained Solutions for Displacement Field

As discussed in detail in Chapter 8, there are compatibility constraints which relate the various components of the strain tensor. It is not a priori evident that there exist continuum solutions which satisfy the rather rigorous demands that the infinite anisotropy approximation imposes, i.e. $e_1 = e_2 = 0$. In other words, it must be proven that there exists a (non-trivial) class of displacement fields which satisfies the compatibility condition in this constrained limit. In fact, we shall now show that such a class does exist, and moreover that this class of constrained solutions is naturally related to the tweed deformation.

First, we consider the two dimensional case. The infinite anisotropy constraints in this case take the form
\[ e_1 = \frac{(e_{xx} + e_{yy})}{\sqrt{2}} \sim \partial_x U_x + \partial_y U_y = 0 \quad (5.1a) \]
\[ e_2 = \frac{(e_{xy} + e_{yx})}{2} \sim \partial_y U_x + \partial_x U_y = 0. \quad (5.1b) \]

Changing variables to

\[ s = x + y \quad \text{and} \quad t = x - y \quad (5.2) \]

and writing the displacement field \( U = (X(x, y), Y(x, y)) \) in terms of the new variables \( U = (X(s, t), Y(s, t)) \) allows us to reexpress these constraints

\[ (\partial_s + \partial_t)X + (\partial_s - \partial_t)Y = 0 \quad (5.3a) \]
\[ (\partial_s - \partial_t)X + (\partial_s + \partial_t)Y = 0. \quad (5.3b) \]

Adding and subtracting these, we find

\[ \partial_s(X + Y) = \partial_t(X - Y) = 0, \quad (5.4) \]

and therefore \((X + Y)\) is a function of the variable \( t \) only, and \((X - Y)\) is a function of the variable \( s \) only. The immediate result is

\[ U = \begin{pmatrix} 1 \\ -1 \end{pmatrix} U_+(x + y) + \begin{pmatrix} 1 \\ 1 \end{pmatrix} U_-(x - y) \quad (5.5) \]

where \( U_+ \) and \( U_- \) are any arbitrary functions of their arguments.

Before discussing the significance of this simple result, we proceed to derive the analogous result in three dimensions. We first recast the infinite anisotropy constraints

\[ e_1 = \frac{(\partial_x U_x + \partial_y U_y + \partial_z U_z)}{\sqrt{3}} = 0 \quad (5.6a) \]

and
\[ e_{yz} = (\partial_z U_y + \partial_y U_z)/2 = 0 \]  
\[ (5.6b) \]
\[ e_{xx} = (\partial_x U_x + \partial_x U_z)/2 = 0 \]  
\[ (5.6c) \]
\[ e_{xy} = (\partial_y U_x + \partial_x U_y)/2 = 0 \]  
\[ (5.6d) \]
in new variables
\[ s = y + z, \quad t = z + x, \quad \text{and} \quad u = x + y \]  
\[ (5.7) \]
to get
\[ (X_t + X_u) + (Y_u + Y_s) + (Z_s + Z_t) = 0 \]  
\[ (5.8a) \]
and
\[ (Y_s + Y_t) + (Z_u + Z_s) = 0 \]  
\[ (5.8b) \]
\[ (Z_t + Z_u) + (X_s + X_t) = 0 \]  
\[ (5.8c) \]
\[ (X_u + X_s) + (Y_t + Y_u) = 0 \]  
\[ (5.8d) \]
where subscripts denote differentiation. Rearranging these in a useful way we get
\[ X_s + Y_t + Z_u = 0 \]  
\[ (5.9a) \]
\[ (-X + Y + Z)_s = 0 \]  
\[ (5.9b) \]
\[ (X - Y + Z)_t = 0 \]  
\[ (5.9c) \]
\[ (X + Y - Z)_u = 0, \]  
\[ (5.9d) \]
the last three of which immediately yield
\begin{align*}
(-X + Y + Z) &= 2\tilde{S}(t, u) \quad (5.10a) \\
(X - Y + Z) &= 2\tilde{T}(u, s) \quad (5.10a) \\
(X + Y - Z) &= 2\tilde{U}(s, t). \quad (5.10a)
\end{align*}

where \(\tilde{S}(t, u), \tilde{T}(u, s),\) and \(\tilde{U}(s, t)\) are arbitrary functions of the two specified variables, and the factor of two is inserted for later convenience. We can thus express the single component displacement functions \(X, Y,\) and \(Z\) as

\begin{align*}
X(s, t, u) &= \tilde{T}(u, s) + \tilde{U}(s, t) \quad (5.11a) \\
Y(s, t, u) &= \tilde{S}(t, u) + \tilde{U}(s, t) \quad (5.11b) \\
Z(s, t, u) &= \tilde{S}(t, u) + \tilde{T}(u, s) \quad (5.11c)
\end{align*}

and apply constraint \((5.8a),\) to find

\[(\tilde{S}_t + \tilde{S}_u) + (\tilde{T}_u + \tilde{T}_s) + (\tilde{U}_s + \tilde{U}_t) = 0. \quad (5.12)\]

From this we can immediately see that the cross derivative of each of the terms in parenthesis vanishes:

\[
\frac{\partial^2}{\partial t \partial u} (\tilde{S}_t + \tilde{S}_u) = \frac{\partial^2}{\partial u \partial s} (\tilde{T}_u + \tilde{T}_s) = \frac{\partial^2}{\partial s \partial t} (\tilde{U}_s + \tilde{U}_t) = 0, \quad (5.13)
\]

which allows us to separate each of the terms in parentheses into a function of one variable plus a function of the other:

\begin{align*}
(\tilde{S}_t + \tilde{S}_u) &= t(t) + u'(u) \quad (5.14a) \\
(\tilde{T}_u + \tilde{T}_s) &= u(u) + s'(s) \quad (5.14b) \\
(\tilde{U}_s + \tilde{U}_t) &= s(s) + t'(t). \quad (5.14c)
\end{align*}
However, inserting these back into (5.12) tells us that (in the absence of additive constants which merely reflect homogeneous rotations and homogeneous tetragonal strain) we find

\[ t(t) = -t'(t), \quad u(u) = -u'(u), \quad \text{and} \quad s(s) = -s'(s) \quad (5.15) \]

and hence

\[
\begin{align*}
(\tilde{S}_t + \tilde{S}_u) &= t(t) - u(u) \\
(\tilde{T}_u + \tilde{T}_s) &= u(u) - s(s) \\
(\tilde{U}_s + \tilde{U}_t) &= s(s) - t(t)
\end{align*}
\]  

(5.16a)  
(5.16b)  
(5.16c)

Without loss of generality, a function \( f(q, r) \) having the property \( f_q + f_r = q(q) + r(r) \) can be written \( f(q, r) = Q(q) + R(r) + F(q - r) \). Accordingly, we write

\[
\begin{align*}
\tilde{S} &= T(t) - U(u) + \tilde{S}(t - u) \\
\tilde{T} &= U(u) - S(s) + \tilde{T}(u - s) \\
\tilde{U} &= S(s) - T(t) + \tilde{U}(s - t).
\end{align*}
\]  

(5.17a)  
(5.17b)  
(5.17c)

Finally, referring back to Eqs. (5.11) we arrive at the following general expression for the displacement field:

\[
U = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ -1 & 1 & 1 \end{pmatrix} S(y + z) + \begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & 1 \\ 1 & -1 & 0 \end{pmatrix} T(z + x) + \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} U(x + y)
\]

\[
\begin{align*}
&+ \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & 1 & 1 \end{pmatrix} \tilde{S}(y - z) + \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 1 & 1 & 0 \end{pmatrix} \tilde{T}(z - x) + \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tilde{U}(x - y).
\end{align*}
\]  

(5.18)

The results given in Eqs. (5.5) and (5.18) give the general form for an arbitrary displacement field of an elastic continuum in the limit of infinite anisotropy. Perhaps the most notable feature of these constrained solutions
is that they represent drastically restricted subspaces of the entire space of displacement fields. Eq. (5.5), represents a superposition of two one-dimensional modulations ($U_+$ and $U_-$) and Eq. (5.18) represents a superposition of six one-dimensional modulations ($S$, $T$, $U$, $S$, $T$, and $U$). If $N$ is the linear system size, then in two dimensions, the solution space has essentially been reduced from $2N^2$ degrees of freedom to $2N$ degrees of freedom, and in three dimensions, from $3N^3$ down to $6N$: a reduction so ruthless that it seems to leave little hope that an interesting answer to the rather demanding tweed problem can be found within this drastically constraining approximation.

Still, there is some promise that this will amount to an illuminating approximation. First, the form of the displacement fields represented by the constrained solutions (5.5) and (5.18) are precisely of the tweedy type. As discussed in Chapter 3 and Chapter 7, electron and x-ray diffraction tell us that tweed is composed of $(110)/\{\overline{1}0\}$ shears. Each of the one-dimensional modulations in Eqs. (5.5) and (5.18) is one of the available $(110)/\{\overline{1}0\}$ modes. (There are two symmetrically equivalent modes in two dimensions and six in three dimensions.) More visually, these constrained displacement fields are naturally diagonal in appearance, and correspond nicely to the real space TEM images of tweed.

Second, when the limit of infinite anisotropy is relaxed and elastic parameters for real materials are used, the solutions found in simulations, ours and others$^{103,68}$, are reassuringly similar to the constrained solutions. The deformations are very nearly superpositions of the expected one-dimensional modulations, where instead of infinite correlations along the transverse direction, there are very extended, anisotropic correlations.
Third, although the constrained solutions are only a limited subspace of the total solution space, it is a subspace which is important to the question of pretransitional deformations. One of the premises of this research is that compositional variation causes the transformation temperature to spatially vary, and that pretransitional effects occur as a result of atomic scale regions deforming prematurely into the martensitic phase. Even within the set of constrained solutions, it is possible in two dimensions to construct deformations which cleanly modulate between the austenite and the martensitic variants without building up any long-range strain or creating awkwardly strained domains, (i.e. regions of neither austenite nor martensite). The deformations are constructed in the following surprisingly simply way.

Martensitic variants have $\phi = \pm \phi_0$ (where $\phi_0$ is the net rectangular strain in the martensitic phase), and the undeformed austenite has $\phi = 0$. A modulation consisting solely of the values $\phi = (0$ or $\pm \phi_0)$ must be constructed from a function which Eq.(5.5) implies must have the form

$$\phi(x, y) = \phi^+(x + y) + \phi^-(x - y).$$

This is simply accomplished by taking $\phi^+$ and $\phi^-$ modulations which flip between $-\phi_0/2$ and $\phi_0/2$. The sum will then be a (tweedy!) quilt of austenite and martensite domains.

In three dimensions such a simple construction does not exist. In fact, in general there does not exist an interface along which the austenite phase can join seamlessly with a single martensitic variant. (The FCC $\rightarrow$ HCP transformation is an exception.) As was explained in a general way by the crystallographic theory of martensitic transformations\textsuperscript{104,105}, the austenite–martensite interface (or habit plane) can only form along an invariant plane, which in gen-
eral exists only when the martensitic phase appears as a twinned structure. However, the basic assumption of this theory, that a *macroscopically* invariant plane must exist in order that the austenite-martensite combination does not generate long-range elastic strains, need not be so rigidly adhered to in the case of the mesoscale pretransitional structures which we are studying. Long-range strain need not be prevented through the perfect matching of interfaces, rather it can be accommodated by subtly modulating between phases and variants. In other words, it is not necessary that an atomic scale deformation be a scaled-down version of a macroscopically viable structure. For this reason, a deformation presumably can be constructed which manages to avoid long-range strain by modulating predominantly between austenite and martensite, with occasional necessary contortions\textsuperscript{106}.

### 5.2 Frustration in Tweed

We have pointed out above that the order parameter field, even in the constrained approximation, is capable of modulating between the austenite and the martensitic variants and responding to the local preference for one phase or the other. However satisfying the local preferences is a non-trivial task, and within the geometrical constraints of the system, the randomness is a source of inescapable frustration. Figure 5.1 demonstrates in a very simple and schematic way the essence of the frustration in this system and also in an Ising spin system to which we will be drawing extensive analogies.

On the right, we have three representative Ising spins, $s = \pm 1$, which form a small cluster in a larger system. They are connected by bonds, each of which might prefer parallel (Ferromagnetic) or antiparallel (Antiferromagnetic) alignment. In a spin glass, the bond type (i.e., whether A or F) is set at
random, making it impossible to satisfy all of the bonds. As a demonstration of this, let us attempt to satisfy the bonds as chosen in the figure. If we start at the lower left corner of the triangle, starting (arbitrarily) down, and move around clockwise, we can satisfy each bond in turn. However, for any loop with an odd number of antiferromagnetic bonds, one bond must be broken (in its high-energy state): here the ferromagnetic bond connecting the bottom two spins is not satisfied.

On the left of Figure 5.1, we have schematically shown the analogous situation for the martensitic system. Four spatially separated regions in the material are shown, and each is marked by the phase that it prefers as a result of the random local composition. For the constrained solutions we are considering, the order parameter $\phi(x, y)$ at each site is a sum of contributions from the modulations $\phi^+(x+y)$ and $\phi^-(x-y)$ (see Eq. (5.19)). The two diagonals along which $\phi^+$ must be specified to determine $\phi(x, y)$ at the four sites, and the two along which $\phi^-$ must be specified, are indicated in the diagram. The task is to specify those four values such that the appropriate pairs sum to values of $\phi$ which satisfy the local strain requirements at the four sites. Starting at the bottom, we have a region which favors the square Austenite phase, so by (arbitrarily) choosing the contribution for the lower left diagonal $+\phi_0/2$ (represented by a plus spin $\uparrow$), the contribution for the lower right diagonal is fixed to be $-\phi_0/2$ ($\downarrow$) in order to satisfy the local free energy in the bottom site: $\phi = 0$, represented by the square box surrounding the A. Again, moving clockwise, we can satisfy the free energy in the left-hand site (which prefers Martensite) by choosing $+\phi_0/2$ ($\uparrow$) for the upper left diagonal, leading to a net order parameter $\phi_0$ and a short-fat rectangular deformation. We can continue this process through the top site, but when we reach the final, right-hand site, the order
Figure 5.1  A schematic representation of frustration in the tweed system (left) and the spin glass system (right). Each loop has an odd number of A bonds, and therefore must have an unsatisfied bond.
parameter is already determined to be \( \phi = +\phi_0/2 - \phi_0/2 = 0 \) (†): the local free energy, which prefers \( \mathbf{M} \), is not satisfied.

This is the nature of the frustration in these two systems. The \( \mathbf{A} \)'s in both systems effectively function as antiferromagnetic bonds, so any closed loop with an odd number of \( \mathbf{A} \)'s is frustrated. This frustration is a property of the geometry of the systems along with the fact that random probability will inevitably make perverse choices (and place odd numbers of \( \mathbf{A} \)'s in closed loops). Note, this frustration is not a spurious artifact of the constrained solution; we cannot claim that our inability to find a solution results from having an inadequate number of degrees of freedom at our disposal, for in both examples the number of degrees of freedom was equal to the number of random constraints which needed to be satisfied. It is geometry which confounded attempts to find a solution by insinuating additional implicit constraints into the picture.

5.3 Mapping Tweed onto a Spin Glass

The important similarity between the tweed system and the spin system has thus been established. The two systems have frustration and disorder in common, and therefore have the two ingredients which together give rise to glassy behavior\(^{107}\). In this section, we will strengthen the claim that tweed is glassy by formally mapping the tweed system onto an Ising spin glass Hamiltonian.

As suggested by the previous arguments, the equivalent of the “bonds” in the tweed system are spatially localized regions, whose well defined preference for one phase or the other determines the bond’s sign. A “site” in the tweed system is an entire diagonal (somewhat counterintuitively), along which the function \( \phi^+ \) (or \( \phi^- \), depending on the orientation of the diagonal) will take some fixed value, either \(-\phi_0/2\) or \(+\phi_0/2\). The underlying physics of the model
is the structural phase transition which the system is undergoing, guaranteeing that there are only three stable strain configurations in which any region will want to sit (austenite, or two martensitic variants). Energetic considerations will therefore force the order parameter modulations $\phi^+$ and $\phi^-$ to be double valued ($-\phi_0/2$ or $+\phi_0/2$), allowing us to equate them with sets of Ising spins. We will denote the value of the function $\phi^+$ along a diagonal $i = x + y$ by $\phi_i^+$, and similarly $\phi_j^- \equiv \phi^-(j = x - y)$, where $i$ and $j$ take on integer values and enumerate all the sites $\{i, j\}$ in the lattice.

The bond strength and sign will be determined by the difference in free energy of the austenite and martensite configurations at a given site: $f_A(\eta(i,j)) - f_M(\eta(i,j))$ (or more concisely, $(f_A - f_M)(i,j)$). If austenite is the preferred phase this quantity is positive, and an antiferromagnetic bond exists between $\phi_i^+$ and $\phi_j^-$. Similarly, a stable martensitic site leads to a ferromagnetic bond. An explicit mapping between the elastic free energy and the spin glass Hamiltonian can now be derived: first write the elastic free energy by rewriting Eq. (4.21)

$$F = \sum_{ij} f(\phi(i,j)) = \sum_{ij} \frac{A_0(i,j)}{2} \phi^2(i,j) - \frac{B_0}{4} \phi^4(i,j) + \frac{C_0}{6} \phi^6(i,j)$$

(5.20)

by rewriting Eq. (4.21)

$$A_\phi(i,j) = A^{\text{crit}}_\phi + A_\phi(\bar{\eta}) + \delta A_\phi(i,j).$$

(5.21)

Here, $A^{\text{crit}}_\phi$ is the critical “temperature”, at which $f_A = f_M$. The coefficient $A_\phi(\bar{\eta})$ reflects the mean quadratic coupling (measured relative to $A^{\text{crit}}_\phi$) at the nominal composition: positive will favor austenite and negative will favor martensite. The random disorder is contained in the term $\delta A_\phi(i,j)$. For the values $\phi(i,j) = (0 \text{ or } \pm \phi_0)$, we have

$$\frac{A^{\text{crit}}_\phi}{2} \phi^2(i,j) - \frac{B_0}{4} \phi^4(i,j) + \frac{C_0}{6} \phi^6(i,j) = 0$$

(5.22)
allowing us to write

\[ F = \sum_{ij} (A_\phi(\eta) + \delta A_\phi(i, j)) \phi^2(i, j) = \sum_{ij} \frac{(f_A - f_M)(i, j)}{\phi_0^2} \phi^2(i, j). \]  

(5.23)

In the constrained approximation we have \( \phi(i, j) = \phi_i^+ + \phi_j^- \) which gives us

\[ \sum_{ij} \frac{(f_A - f_M)(i, j)}{\phi_0^2} (\phi_i^{+2} + \phi_j^{-2} + 2\phi_i^+\phi_j^-) \]  

(5.24)

which we can more concisely write

\[ \sum_{ij} f_{ij} \phi_i^+\phi_j^- \]  

(5.25)

where we’ve put \( f_{ij} = 2(f_A - f_M)(i, j)/\phi_0^2 \) and redefined the zero energy so we can drop the constant terms. This is now expressly written as a spin glass Hamiltonian. In particular, noting that the \( \phi \) are partitioned into two distinct seas of spins, \{\( \phi^+ \)\} and \{\( \phi^- \)\} and that interactions occur between every pair \( (\phi_i^+, \phi_j^-) \) and only pairs \( (\phi_i^+, \phi_j^+) \), we can equate this with the well studied antiferromagnetic bipartite \(^{108}\) Sherrington-Kirkpatrick\(^{109,110}\) spin glass.

Furthermore, we mention that the terms which we have let inconspicuously disappear from the initial constrained free energy can also be mapped onto analogous spin system terms. First, the coupling \( \phi(\partial_x^2 - \partial_y^2)\eta \) exerts a force favoring one martensitic variant over the other, (see Appendix A and Chapter 9). This random biasing term, \( (F^- - F^+)\phi(i, j) \) is equivalent to a random internal field which biases the local magnetization toward one spin or the other, adding to the spin glass Hamiltonian a random field term\(^{111}\):

\[ \sum_{ij} H_{ij}(\phi_i^+ + \phi_j^-) \]  

(5.26)

Second, the gradient term \( (\nabla\phi)^2 \) adds ferromagnetic bonds (with no disorder) to the spin model, smoothing out the lattice scale discreteness which
otherwise results:

\[-\kappa \sum_i \phi_i^+ \phi_{i+1}^+ - \kappa \sum_j \phi_j^- \phi_{j+1}^- . \tag{5.27}\]

The behavior of the bare spin glass model Eq.(5.25) accords satisfyingly with the expected tweed behavior - a gratifying vindication of infinite anisotropy approximation. The presumed solution is given by the phase diagram in Figure 5.2, where \(J_0\) is the mean bond strength, and \(J\) is the strength of the randomness, (i.e. the width of a gaussian probability distribution for the bonds.) The solution in the replica symmetric approximation\textsuperscript{108}, not surprisingly, is precisely analogous to the replica symmetric solution of the original Sherrington-Kirkpatrick spin glass, but mirrored about the axis \(J_0 = 0\) since the bipartite model allows both ferromagnetic and antiferromagnetic bonds. When the sites are predominantly austenite-favoring, the system is “antiferromagnetically ordered”: \(\phi^+ = \phi_0/2\) and \(\phi^- = -\phi_0/2\), say, and there is long-range austenitic order and zero net strain \(\phi\). When the sites are predominantly martensite-favoring, the system is “ferromagnetically ordered”: both \(\phi^+\) and \(\phi^-\) equal \(+\phi_0/2\), say, and long-range martensitic order develops as a single strained martensitic domain forms with \(\phi = \phi_0\). Sufficiently close to the martensitic transformation temperature the mean bond \(J_0\) (or \(\bar{A}_\phi\)) is comparable to the randomness \(J\) (or \(\delta A_\phi\)) and the disorder becomes important. Here, some sites are austenite-favoring and some martensite-favoring, and the lattice exerts a frustrated effort to accommodate the local disorder, i.e. tweed is formed. Woven together from austenitic regions and martensitic regions of both variants, there is no long-range spatial order and therefore no macroscopic strain, but the glassy nature of the configuration will manifest itself as long-range order in time and a non-zero Edwards-Anderson order parameter (measured over the
Figure 5.2  Phase diagram\textsuperscript{108} for Antiferromagnetic Bipartite Sherrington–Kirkpatrick spin glass\textsuperscript{109,110}. 
strain field $\phi(i,j)$. There is a brief intermediate thermodynamically stable glass phase lurking between the two conventional phases.

In the spin glass model, the temperature $T$ and the mean bond strength $J_0$ are independent parameters, and the phase diagram is meaningful for all points $(T, J)$. Materials displaying tweed have a mean bond strength $\bar{A}_\phi$ which is temperature dependent: higher temperature gives more austenite-favoring sites. An actual material, then, will trace a path through the phase diagram in Figure 5.2 as shown by the dashed line: from martensite through tweed to austenite as temperature is increased.

The Figure 5.2 is referred to as the “presumed” phase diagram because the replica symmetry broken solution has not been carried out, to our best knowledge. The analysis would be a purely academic exercise, as the predictable solution would simply mimic the replica symmetry breaking result of the Sherrington–Kirkpatrick model\textsuperscript{110} with the appropriate reflection across the $J_0 = 0$ axis. The ferromagnetic magnetized spin glass phase (FMSG) uncovered by the replica symmetry broken analysis would presumably find an antiferromagnetic magnetized spin glass (AFMSG) twin in the bipartite model (as is found on the Bethe lattice\textsuperscript{112}). These phases have long-range magnetic order in space, as well as glassy long-range order in time. A tweedy, glassy mesostructure superimposed on the austenite may be hard to distinguish from the tweed phase itself, however, experimentalists do observe tweed superimposed on already transformed regions of samples. This suggests the intriguing possibility that tweed as a magnetized spin glass also exists!

In three dimensions, the disorder remains and the frustration probably worsens, so we strongly suspect that glassy behavior will persist. The mapping to an
Ising spin glass clearly does not carry over, and it is unclear whether a simple spin model can capture the glassy nature of the three dimensional system: the order parameter now has two components and three martensitic minima in addition to the austenitic minima, and the constrained solutions consist of six one dimensional modulations. Perhaps a more direct approach toward studying the glassiness of tweed will be to build on existing research which seeks to interpret pretransitional mesostructure in terms of interacting elastic dipoles\textsuperscript{113,114,115}.

Reflecting for a moment on the infinite anisotropy approximation, we point out that the infinite diagonal correlations demanded by the constrained solutions translate, in the spin analogy, to the interaction of each $\phi^+$ spin with each $\phi^-$ spin, i.e. an infinite range interaction. The infinite anisotropy approximation, then, amounts to a mean field approximation. We see from experiment and simulation that the correlations are indeed long-range, tens or hundreds of lattice constants, and tweed might be very accurately described by this mean field approximation. We know, for example, that in the rather successful BCS theory of superconductivity Cooper pairs overlap with $\sim 10^6$ other Cooper pairs\textsuperscript{116}. As we have interactions with $L/\xi \sim 50$ other "spins," we maintain a (guarded) optimism about our mean field findings, and carry on with our investigation of tweed, now relaxing the infinite anisotropy limit.
Chapter 6
Numerical Simulation of Unconstrained Tweed

In the previous chapter, the approximation of infinite anisotropy was introduced in order to make the two dimensional tweed model solvable. In this chapter we proceed beyond that mean field approximation, discarding the infinite anisotropy approximation we here consider the full unconstrained free energy as given in Chapter 4. As a check on the general predictions of the analytical spin glass solution, and also to allow us to compare this disorder-driven model to experimental observation, we have developed a numerical simulation of the two dimensional tweed model using real (finite anisotropy) materials parameters. This chapter explains the simulation in detail, and presents its results.

Figures 6.1, 6.2, and 6.3 show the evolution of the simulated system as temperature is lowered, from the undeformed austenite phase, through a pre-transitional regime, into the fully developed martensite phase. One immediately recognizes the telltale diagonal modulations of tweed developing in the pretransitional regime. The simulation reveals that the system does indeed accommodate the energetic demands of the compositional disorder by generating a deformation as shown, i.e. the tweed modulation is the natural response of the system to the disorder.

The simulation consists of numerically solving the continuum system introduced in Chapter 4, discretized onto a square mesh. The simulation variables are the displacements $U_x$ and $U_y$ at each site, which are used to calculate the strains and thus the free energy developed in Chapter 4. A random composition field is assigned at the beginning and held static. A Monte Carlo simulated annealing algorithm is used to minimize the energy, and to generate a stable low
Figure 6.1 Configurations Generated by Numerical Simulation (See text for explanation.)
Figure 6.2  Configurations Generated by Numerical Simulation (See text for explanation.)
Figure 6.3 Configurations Generated by Numerical Simulation (See text for explanation.)
energy configuration for a given point in parameter space. The shading in the
diagrams reflects the strain order parameter \( \phi(x) \), varying from blue to red as
the strain goes from the horizontally stretched rectangular martensite variant,
to undeformed square phase, to the vertically stretched variant.

6.1 Calculation of Strains:

The continuum simulation is discretized onto a square \( N \) by \( N \) lattice,
where typically we have used \( N = 51 \). From the displacements of the four
corners of given cell, we calculate the corresponding strain tensor according to
a straightforward finite differences method. For example, the cell bounded by
the points \((x, y), (x+1, y), (x, y+1), \) and \((x+1, y+1)\) has strains

\[
\partial_x U_x(x, y) = \frac{1}{2} \{ \frac{U_x(x+1, y+1) - U_x(x, y+1)}{a} + \frac{U_x(x+1, y+1) - U_x(x, y+1)}{a} \}
\]

(6.1)

and

\[
\partial_y U_x(x, y) = \frac{1}{2} \{ \frac{U_x(x, y+1) - U_x(x, y)}{a} + \frac{U_x(x+1, y+1) - U_x(x+1, y)}{a} \}
\]

(6.2)

(where \( a \) is the mesh size) and similarly for \( \partial_y U_y(x, y) \) and \( \partial_z U_y(x, y) \). The
fully irrotational strain tensor

\[
\epsilon_{ij} \equiv \frac{1}{2} (\partial_i U_j + \partial_j U_i + \partial_i U_1 \partial_j U_1)
\]

(6.3)

is calculated accordingly, and thence the strain fields \( \epsilon_1, \epsilon_2 \) and \( \phi \) from
Working on a mesh with a square cell gives us a total of eight degrees of freedom (four points times two displacement directions) to describe the deformation of a single cell. In Eqs. (6.4), three of those degrees of freedom have been equated with the components of the strain tensor, and are therefore ultimately accounted for in the free energy. The remaining five modes, if not adequately taken into consideration, will be uncontrolled deformations in the simulation lattice, and the resulting configurations will be overwhelmed by possibly meaningless deformation modes. Figure 6.4 depicts all eight of the displacement modes in a convenient basis. Three are accounted for by the strains \( \varepsilon_1, \varepsilon_2 \) and \( \phi \). Two more are pure translations and one a pure rotation, which appropriately do not incur free energy costs. The remaining two modes, unlike the other six modes, are inhomogeneous deformations, corresponding to gradients of the \( \phi \) strain

\[
S_1 = \partial_t^2 U_s = \partial_t \phi + O\left(\frac{\xi}{L}\right) \tag{6.5a}
\]

\[
S_2 = \partial_s^2 U_t = \partial_s \phi + O\left(\frac{\xi}{L}\right) \tag{6.5b}
\]

(where the variables \( s = (x + y)/\sqrt{2} \) and \( t = (x - y)/\sqrt{2} \) are used for clarity.) These modes correspond to twin boundaries between the two martensitic variants: \( S_1 \) is a boundary in the (11) direction and \( S_2 \) in the (1\bar{1}) direction. Therefore, these modes are indeed accounted for, via the free energy term which is a gradient of \( \phi \).
Figure 6.4  Four points in two dimensions define eight displacement degrees of freedom. Three of these deformation modes are strains which appear in the free energy. Three of them are symmetries (two translational and one rotational) which should be transparent to the free energy. Two are inhomogeneous deformations corresponding to strain gradients.
6.2 Materials Constants

We have chosen FePd as a model material to supply the parameters needed in the numerical simulation. An interesting material for its shape memory property, it also has a well studied tweed regime\textsuperscript{56,60,61} and the various relevant parameters have been well characterized.

Static harmonic elastic constant measurements\textsuperscript{62} have given us \( A_1 = C_{11} + 2 C_{12}, \ A_2 = 4 C_{44}, \) and \( A_\phi = 2 C' \) at the onset of the tweed regime. The coefficients \( B_\phi \) and \( C_\phi \) are determined by requiring that the known martensitic strain \( \phi = \phi_0 \) and the austenite \( \phi = 0 \) both have a free energy value of zero, and are both extrema, at the known critical value of \( A_\phi \). The coupling to temperature, \( A_T \) is known from measurements\textsuperscript{62} of the temperature dependence of \( A_\phi \). The coupling to statistical compositional variations, \( A_\eta \), will be discussed in detail below.

The strain gradient parameter \( \kappa \) can be calculated from the curvature of the TA\textsubscript{1} phonon dispersion curve near the Brillouin zone center. A positive strain
gradient coefficient will contribute upward curvature, as seen in experiment\(^4\).

To illustrate this point in a simple model, consider a one dimensional continuum with strain and strain gradient contributions to the free energy:

\[
f = \frac{\alpha}{2} (u_x)^2 + \frac{\beta}{2} (u_{xx})^2.
\] (6.6)

For a normal mode of the form \(U(x, t) = U_0 e^{i(kz - \omega t)}\) we see that the equation of motion,

\[
\rho \ddot{U}(x) = -\frac{\delta f}{\delta U(x)},
\] (6.7)

leads to

\[
\omega^2 = \frac{\alpha}{\rho} k^2 + \frac{\beta}{\rho} k^4
\] (6.8)

and therefore an upward curvature in the otherwise linear dispersion relation.

In a discrete system, the derivatives are replaced by finite differences, and the resulting dispersion relation is therefore

\[
\omega^2 = \frac{\alpha}{\rho} \left( \frac{\sin k a}{a} \right)^2 + \frac{\beta}{\rho} \left( \frac{\sin k a}{a} \right)^4.
\] (6.8)

We can do the same calculation for the two dimensional system, where

\[
f = \frac{A_\phi}{2} \phi^2 + \frac{\kappa}{2} (S_1^2 + S_2^2).
\] (6.9)

Using variables \(s = (x + y)/\sqrt{2}\) and \(t = (x - y)/\sqrt{2}\) this can be rewritten

\[
f = \frac{A_\phi}{2} \left( \frac{U_{st} + U_{ts}}{\sqrt{2}} \right)^2 + \frac{\kappa}{2} (U_{stt} + U_{tss})^2.
\] (6.10)

Since ultimately we would like to compare to the measured phonon dispersion for the TA\(_1\) branch, we will consider the normal mode

\[
\bar{U}(x, t) = U_0 \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{i(kz - \omega t)}.
\]
which is a (11)/(11) shear wave. This conveniently reduces to a one dimensional problem essentially identical to that above, since the displacements are entirely along the \( \hat{i} \) direction. The dispersion relation is correspondingly

\[
\omega^2 = \frac{A_\phi k^4}{2\rho} + \frac{\kappa}{\rho} k^4.
\]

(6.11)

Returning to our discretization scheme, where \( \phi, S_1, \) and \( S_2 \) are defined in terms of relative positions of neighboring points, we will be able to better compare the calculated dispersion curve to the experimentally measured one (which is, after all, measured on a real discrete system). We find

\[
\omega^2 = \frac{A_\phi}{\rho} \left( \frac{\sin \sqrt{2} k a}{a} \right)^2 + \frac{4\kappa}{\rho} \left( \frac{\sin \frac{\sqrt{2} k a}{a}}{} \right)^4.
\]

(6.12)

Using this expression, we fit to experimental inelastic neutron scattering data\(^{117}\) for the TA\(_1\) phonon dispersion curve in FePd to find the value of \( \kappa \) given in table 6.1.

The mesh size \( a \) of the simulated system can correspond to the lattice scale, but does not have to. Since computer power is at a premium, and since we are investigating a mesoscale behavior, it is more efficient to only discretize down to a mesh size which corresponds to the length scale of the deformations. Indeed, we must discretize at least down to this scale in order for a continuum approximation to remain valid. The elastic constants \( A_\phi, A_1, A_2, B_\phi \) and \( C_\phi \) do not depend on the scale. However, \( \kappa \) must be divided by the mesh size squared, to account for the scaling of the gradient term, and \( A_\eta \cdot \delta \eta \) must be divided by the mesh size, to account for the scaling of the \( 1/\sqrt{N} \) statistical composition variations. As it turns out, the deformation is occurring on a fairly small length scale, and we've chosen a meshsize corresponding to the lattice constant for most of our simulations, and for all of the data given here.
6.3 Monte Carlo Algorithm

The objective of the numerical simulation is, of course, to find a low energy configuration corresponding to a particular set of parameters and a given realization of the quenched disorder. After experimenting with a conjugate gradient method, it quickly became clear that the inherent glassiness of the problem required the flexibility of a Monte Carlo simulated annealing algorithm\textsuperscript{118}. We have adapted the standard Metropolis algorithm to make use of the known properties of our free energy functional.

Instead of the standard acceptance rate:

\[ P(\Delta E) = \min(1, e^{-\beta \Delta E}) \]

we make use of the fact that the calculated energy difference \( \Delta E \) can easily be broken up into two pieces: one piece \( \Delta E_0 \) which contains the terms linear in the size of the attempted step, and another part \( \Delta E_1 \) which contains all terms of higher order. For a given step, \( \Delta E_0 \) is calculated, and the step is accepted conditionally with probability

\[ P_0(\Delta E_0) = \min(1, e^{-\beta \Delta E_0}). \]

If the step survives this conditional acceptance, then \( \Delta E_1 \) is calculated and the step is finally accepted with probability

\[ P_1(\Delta E_0) = \min(1, e^{-\beta \Delta E_1}). \]

Since \( \Delta E_0 \gg \Delta E_1 \), the ultimate acceptance or rejection is determined primarily by \( \Delta E_0 \), which is much more easily calculated than \( \Delta E_1 \). This algorithm allows us to reject many moves without having to perform the more computationally intensive calculation of \( \Delta E_1 \).
We can be assured that detailed balance is indeed obeyed by noting

\[
\frac{P(A \rightarrow B)}{P(B \rightarrow A)} = \frac{P_0(\Delta E_0)P_1(\Delta E_1)}{P_0(-\Delta E_0)P_1(-\Delta E_1)} \\
= \frac{\min(1, e^{-\beta \Delta E_0})\min(1, e^{-\beta \Delta E_1})}{\min(1, e^{-\beta \Delta E_0})\min(1, e^{-\beta \Delta E_1})} \\
= e^{-\beta \Delta E_0} \cdot e^{-\beta \Delta E_1} \\
= e^{-\beta \Delta E}
\]

Typically, we quench more than four decades of temperature, using fifteen thousand attempted Monte Carlo steps per lattice site per decade.

6.4 Phase Diagram

A phase diagram, Figure 6.5, generated by the simulation, is straightforward and intuitively sensible. The vertical axis is the mean elastic constant $\bar{A}_q$ at the nominal composition. Since $\bar{A}_q$ softens linearly with temperature over a large temperature range (at least $62150^\circ K$), this axis also effectively reflects temperature. The horizontal axis is the strength of the coupling, $A_\eta$, between the strain order parameter $\phi$ and the composition inhomogeneity, $\delta \eta$. The horizontal axis is not simply the average composition, as is usually the case for binary alloy phase diagrams. Over the range of interest, composition has a simple relationship to transformation temperature, and so no additional information would be revealed. The strength of the coupling reveals more information, and is a more appropriate comparison to the analysis of Chapter 5, as will be discussed below. The general structure of the phase diagram is good confirmation of the general mechanism underlying our model: sufficiently far from the thermodynamic transformation temperature for the nominal composition,
Figure 6.5  Phase Diagram for this model is plotted against parameters $\bar{A}_\phi$ and $A_\eta$. It contains three important regimes: 1) The AUSTENITE phase is the relatively undeformed lattice. 2) The TWEED structure develops as a response to the compositional disorder. The degree of deformation depends on the degree of softening and the strength of the coupling to the disorder field. 3) The TWINNED MARTENSITE is the conventional low temperature phase. The dotted line corresponds to the phase boundary in the infinite anisotropy approximation which maps the martensitic tweed problem to a spin glass. (See Chapter 5.)
the expected conventional phases appear, while near to the transformation temperature there is a region where the effect of the disorder becomes important, the lattice deforms, and tweed appears.

In experimental observations\textsuperscript{62}, as the temperature of a sample is lowered toward the martensitic transformation temperature, a smooth and unremarkable TEM image gives way to a mottled pattern which signals the onset of some static lattice distortion — static at least on the (several second) time-scale of TEM observations. With further decrease in temperature, the mottled pattern organizes into a pattern with a distinguishable directionality, acquiring a noticeable but diffuse tweediness. As the transformation temperature is approached, the tweed develops increasingly coarse and long-range correlations. As the sample passes through the martensitic transformation, the tweed gives way to fully transformed martensite, perhaps nucleating the emerging finely twinned structure\textsuperscript{†}.

In direct correspondence with these experimental observations, the simulation yields precisely this same progression of pattern development as \( \bar{A}_\phi \) is decreased, (where \( A_\eta \) is held fixed at some constant value). The images 6.1 through 6.3 show the evolution of the simulated system as the temperature is lowered. A perfectly undeformed system (6.1a) is initially interrupted by scattered, non-interacting and uncorrelated regions of distortion (6.1b). These are regions which have relatively large values of \( \delta \eta \) (large negative values, since \( A_\eta \) is positive for FePd) and are deforming precociously toward the martensitic phase. As \( \bar{A}_\phi \) is further lowered, these regions become dense enough to inter-

\textsuperscript{†} The twins form for precisely the same reason that domains form in ferromagnets: elastic strain energy (magnetic field energy) is minimized by setting up alternating martensitic variants (magnetic domains) which partially cancel each other's long-range strain field (magnetic field).
act, and longer range diagonal correlations develop, yielding a diffuse tweed (6.2a) which grows increasingly distinct (6.2b). As $A_\phi$ approaches the nominal transformation temperature of the sample, an increasing fraction of the sample prefers the martensitic phase, and the tweed grows very coarse (6.3a) before finally transforming into the twinned martensite configuration (6.3b).

The parameters in this phase diagram are $A_\phi$ (or equivalently, temperature) and the strength of the coupling to compositional variations, $A_\eta$. In the laboratory, temperature is easily varied, but for any given alloy the coupling strength is an unadjustable property of the material, so the behavior of a sample will trace a trajectory through the phase diagram which falls along a single line, presumably with essentially constant $A_\eta$. (Alternately, holding temperature fixed, the behavior of a material may be investigated over a range of $A_\phi$ by studying several samples over a range of nominal compositions, $\bar{\eta}$.) By comparing the electron microscopy observations of FePd to the phase diagram derived from simulations, we determine the effective value of $A_\eta$. In experimental investigations of FePd$^{62}$ the onset of tweed is seen to be roughly one hundred degrees above the transformation temperature, corresponding to $A_\phi = 4 \cdot 10^{10} \frac{N}{m^2}$. By matching to the experimentally observed tweed range, we determined the strength of the coupling to composition variation required to generate tweed over this range in our simulation; the value found is $A_\eta \approx 2.0 \cdot 10^{10} \frac{N}{m^2}$. This figure may be compared to the following somewhat simplistic estimate for $A_\eta$: If, say in a binary alloy such as FePd, the full "bulk" composition variation $(dA_\phi/d\bar{\eta})$ coefficient were assigned to each lattice site, and the composition at each simulation site varied between pure Fe or Pd, the statistical fluctuation of $A_\phi$ would be 50 times larger than that found to be required in our simulations. This result should be regarded in the light that there is apparently plenty of
driving force provided by simple compositional variations to produce tweed, even in the absence of any specific defects or reconstructive, order–disorder changes.

This rather large estimate for the coupling $A_\eta$ neglects several important points which should be considered in any careful attempt to calculate the coupling to composition: 1) $dA_\phi/d\bar{\eta}$ is the product of $dT_M/d\bar{\eta}$ and $dA_\phi/dT$, where each of these are known from experimental measurements near $T_M$. Linearly extrapolating away from the range of $\bar{\eta}$ (29% to 32%) over which the martensitic transformation occurs may well overestimate its strength for compositions outside of this range. As mentioned above, it is convenient to think of the martensitic transformation as occurring at a (weakly temperature dependent) critical composition, so it is perhaps more accurate to approximate $A_\phi$ as a step function at the critical composition, say, rather than a simple linear function. 2) As will be discussed further below, finite temperature effects are important in these systems. Thermal lattice vibrations are quite substantial at the temperatures at which tweed is seen, and will be correlated over some temperature dependent length scale, transmitting and averaging out the effects of any disorder, including local compositional variation. 3) In any Landau–Ginzburg theory of a non-uniform system, the existence of a local free energy, (a concept which is thermodynamic in nature,) implicitly assumes that one has “integrated out” certain (secondary) degrees of freedom. For example, defining a free energy functional of a static strain tensor requires integrating over phonon modes, which necessarily introduces a coarse-graining length scale$^{41,119}$. Introducing this length scale into the problem will result in averaging the effect of compositional variations (in addition to changing other parameters). 4) Any physical mechanism which is based on the chemistry of an alloy or doped compound
will involve electronic effects which will exert their influence over a length scale which is larger than the lattice spacing, typically on the order of a fermi length. Again, this will lead to a spatial averaging of composition, weakening the apparent strength of the coupling to local compositional variation. 5) This two dimensional model, although faithful to the real three dimensional material from the perspective of symmetry requirements, neglects an important effect of dimension on compositional fluctuation: a composition field which is defined by averaging within some radius will average over a region of material which whose size will depend on dimension. Correspondingly, in a higher dimension there will be smaller compositional fluctuations.

The dotted lines in the phase diagram (Figure 6.5) are drawn to provide a comparison between the unconstrained numerical simulation and the constrained model presented in Chapter 5 in which the martensitic system was treated analytically by taking the approximation of infinite elastic anisotropy and mapping tweed onto a spin glass. In the spin glass phase diagram, Figure 5.2, the boundaries of the spin glass phase are vertical lines occurring where the mean bond strength $J_0$ and the random bond strength $J$ have a ration equaling one. These vertical boundaries translate into diagonal boundaries with a constant slope of one in Figure 6.5. The numerically determined boundary between tweed and austenite is quite well approximated by the analytically predicted line.

The boundary between the spin glass and the twinned martensite, however, is quite a bit higher than prediction, suggesting the presence of some mechanism which stabilizes the twinned martensite relative to the tweed. This phenomena arises from the fact that the elastic system can relax into slightly strained configurations near the locally stable austenite or martensite minima, in contrast
to the Ising system which is constrained to take values of precisely $+1$ or $-1$.

In reacting to the disorder term in the potential, $\delta A_\phi \phi^2$, it is easily seen that the system can much more effectively relax around the martensitic configuration than the austenite configuration. Local perturbations of size $\delta \phi$ around the (nominal) martensite minima at $\phi = \pm \phi_0$ will yield linear gains in the free energy ($\Delta f = 2\delta A_\phi \phi_0 \delta \phi$) whereas perturbing around the austenite minimum at $\phi = \pm \phi_0$ will yield only quadratic gains, ($\Delta f = 2\delta A_\phi \delta \phi^2$). The system, as a result, can much more easily accommodate disorder in the martensitic phase, and the long range martensitic order is not abandoned in favor of a tweedy configuration unless the disorder is of a very large magnitude. The net effect is that the tweed region of the phase diagram imposes much farther into the (nominal) austenite phase than the (nominal) martensite phase.

In the following chapter, we shall investigate quantitatively the nature of the tweed deformation produced by the numerical simulation.
Chapter 7

Analysis of the Tweed Deformation

Despite the considerable experimental effort toward laying bare the nature of the lattice distortion underlying tweed, and the substantial body of data which has been gathered, tweed still defies an unambiguous quantitative characterization. This chapter hopes to make some steps toward analyzing the tweed structure based on diffraction data. By studying computer generated tweed, we have the opportunity to directly compare the $k$-space and real space information, and therefore better understand the relationship between diffraction observations of tweed and the real space distortion.

Because of the difficulty in using a TEM image to determine the real space deformation underlying an image as complex as tweed, the unambiguous information we have regarding the tweed structure has been extracted primarily from x-ray diffraction data. It has long been known that the diffraction patterns seen in tweed are consistent with the presence of $\{110\}$ planes shearing in $(1\bar{1}0)$ directions$^{58,59}$, the so-called Zener mode$^{69}$. The square $\rightarrow$ rectangular transformation, the cubic $\rightarrow$ tetragonal transformation, and the tetragonal $\rightarrow$ orthorhombic transformations all result from precisely such $\{110\}/(1\bar{1}0)$ shears. In addition, this shear (coupled with an additional homogeneous strain) is responsible for body-centered cubic $\rightarrow$ close-packed transformations. The observation of a pretransitional deformation which involves this particular shear is therefore very consistent with the approach of the martensitic transformation. Furthermore, it is this shear mode that couples to $C'$, the elastic constant which softens in many materials as the martensitic transformation temperature is ap-
proached, and which motivated the approximation of infinite elastic anisotropy discussed in Chapter 5.

We now compare the "x-ray diffraction patterns" of our simulated tweed with experimental diffraction patterns from materials exhibiting tweed, and we look in detail at the nature of the diffraction pattern and analyze it with the aim of extracting from them conclusive information regarding the tweed structure. The simulated diffraction patterns are computed directly by Fourier transforming the displacements computed by the simulation. The resulting diffraction pattern is equivalent to that arising from an infinite periodic sample with a repeating unit identical to our simulation system. We have assumed the structure factors for the A and B atoms in our simulations are identical, and we have ignored their $Q$ dependence. Figure 7.1 shows experimental x-ray diffraction contours taken from tweed produced in YBaCuO, and diffraction patterns at the same Bragg peaks for the simulated tweed. As can be seen, the qualitative features are faithfully reproduced.

Let us now quantitatively relate this diffraction behavior to the lattice displacements. To consider the diffraction pattern from a distorted lattice, we make use of the fact that an arbitrary displacement field can be written in a perfectly general way as

$$U(x, y) = \left( \begin{array}{c} 1 \\ -1 \end{array} \right) U_+ \left( \frac{x + y}{\xi}, \frac{x - y}{L} \right) + \left( \begin{array}{c} 1 \\ 1 \end{array} \right) U_- \left( \frac{x + y}{L}, \frac{x - y}{\xi} \right).$$

In the infinite anisotropy approximation, $L$ would be taken to be infinity, yielding Eq. (5.5). A displacement consisting of long (but not infinite) diagonal

---

$\dagger$ Since we are assuming the presence of compositional inhomogeneities, a more exact diffraction calculation might have allowed structure factors to be species dependent. This effect is likely to be important primarily in martensitic systems in which non-random chemical clustering plays an important role but less so in our model system with only random fluctuations.
Figure 7.1 Diffuse Streaking: around three bragg points is shown. a) Experimental x-ray scattering data\textsuperscript{75} for YBa\textsubscript{2}Cu(Al)\textsubscript{3}O\textsubscript{7-δ} around the indicated Bragg peaks. b) Corresponding diffraction data extracted from the computer simulation of tweed (using FePd parameters) faithfully reproduce important features of the experimental data, i.e. the diffuse streaking is highly anisotropic, most pronounced in the (11) directions, and asymmetrically depends on the Bragg peak index.
correlations can be expressed by taking \( L \gg \xi \) (where we define \( U_- \) and \( U_+ \) such that they have similar functional dependences on their first and second arguments.) The correlation length \( L \) then describes the longitudinal length scale of the tweed striations, and \( \xi \) describes their transverse width.

The general expression\(^{121}\) for the diffracted intensity at a wavevector \( \mathbf{Q} \), (scattering from sites \( s \) with structure factors \( f_s \)) is

\[
I(\mathbf{Q}) = \left| \sum_s f_s(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{R}_s} \right|^2. \tag{7.2}
\]

If we write \( \mathbf{Q} = \mathbf{K} + q \) (where \( \mathbf{K} \) is the nearest reciprocal lattice vector to \( \mathbf{Q} \)) and write \( \mathbf{R}_s = \mathbf{R}_s^0 + \mathbf{U}_s \) (where \( \mathbf{U}_s \) is a displacement around the lattice point \( \mathbf{R}_s^0 \)) then we can expand (7.2) assuming small displacements and find:

\[
I(\mathbf{Q}) = \left| f(\mathbf{Q}) \right|^2 \left| \sum_s (\mathbf{Q} \cdot \mathbf{U}_s) e^{i\mathbf{q} \cdot \mathbf{R}_s^0} \right|^2
\]

(\text{where, recall, we are assuming a material with an effectively constant} \( f_s \)).

Fourier expanding \( \mathbf{U}_s \) and noting that the summation over sites will give us a delta function, we find:

\[
I(\mathbf{Q}) = \left| f(\mathbf{Q}) \right|^2 \left| \mathbf{Q} \cdot \mathbf{U}_q \right|^2. \tag{7.3}
\]

Eq.(7.3) indicates that, in the approximation of small displacements, the intensity of diffuse scattering around Bragg peaks (normalized by \( 1/|f(\mathbf{Q})|^2 \)) will obey a \( |\mathbf{Q}|^2 \) dependence. Comparing the observed scattering intensity to a \( |\mathbf{Q}|^2 \) fit will allow us to verify that the scattering is caused by a small lattice deformation. Substantial deviation from a strict \( |\mathbf{Q}|^2 \) dependence would imply that the approximation of scattering from small displacements is not appropriate, suggesting that the scattering is due perhaps to substitutional disorder or to microdomains large enough to produce size broadening\(^75\). Figure 7.2 shows
the diffuse scattering intensity (normalized by the appropriate structure factor) plotted for Bragg peaks \((0 \; Q \; 0)\), with \(Q/(2\pi/a) = 4, 6, 8, \) and \(10\) for the experimental measurements\(^{75}\) (squares) and \(Q/(2\pi/a) = 0, 1, 2, \ldots 10\) for our simulated diffraction patterns (crosses). The curve shows the best \(|Q|^2\) fit to the experimental data. The minor deviation from the \(|Q|^2\) fit reflects the fact that displacements are finite, yet small.

Assured that we are indeed observing diffuse scattering from small displacements, we can proceed by solving the Fourier transform of Eq.(7.1), \(\tilde{U}(k) = \tilde{U}_+(k) + \tilde{U}_-(k)\), where

\[
\tilde{U}_+(k) = \int \frac{dx \, dy}{\sqrt{A}} \left( \begin{array}{c} 1 \\ -1 \end{array} \right) U_+\left(\frac{x+y}{\xi}, \frac{x-y}{L}\right) e^{i \; k \cdot (x+y)}
\]

\[
\tilde{U}_-(k) = \int \frac{dx \, dy}{\sqrt{A}} \left( \begin{array}{c} 1 \\ 1 \end{array} \right) U_-\left(\frac{x+y}{\xi}, \frac{x-y}{L}\right) e^{i \; k \cdot (x+y)}
\]

Making the substitutions \(k_\pm \equiv (k_x \pm k_y)/\sqrt{2}\) and

\[
s \equiv \frac{(x+y)}{\xi \sqrt{2}}, \quad \text{and} \quad t \equiv \frac{(x-y)}{L \sqrt{2}}
\]

in Eq. (7.4a) and

\[
s \equiv \frac{(x+y)}{L \sqrt{2}}, \quad \text{and} \quad t \equiv \frac{(x-y)}{\xi \sqrt{2}}
\]

in Eq. (7.4b), we find

\[
\tilde{U}_+(k) = \frac{L \xi}{\sqrt{A}} \int ds \, dt \left( \begin{array}{c} 1 \\ -1 \end{array} \right) U_+(s, t) \; e^{i \left(\xi k_+s + Lk_-t\right)}
\]

\[
\tilde{U}_-(k) = \frac{L \xi}{\sqrt{A}} \int ds \, dt \left( \begin{array}{c} 1 \\ 1 \end{array} \right) U_-(s, t) \; e^{i \left(Lk_+s + \xi k_-t\right)}
\]

The general shape of this Fourier transform is clear by inspection: expression (7.5a) is simply the Fourier transform of \(U_+(s, t)\) scaled by \(1/\xi\) along the \(s\) direction and \(1/L\) along the \(t\) direction (similarly for \(U_-\)). Since, by construction, \(U_+\) and \(U_-\) are simple isotropic displacement fields, then so are their
Figure 7.2 The squares are experimental measurements\textsuperscript{75} of diffuse scattering intensity at $Q = (0, Q, 0) + \epsilon$ where $Q/(2\pi/a) = 4, 6, 8, 10$ and $\epsilon = (.06, .06, 0)$. The curve is a fit to $I \sim |Q|^2$, which would be exact in the limit of infinitesimally small displacements. The crosses are simulation data, which have all been scaled by a single constant to best match the data.
Fourier transforms, and the final result is a Fourier transform, $\hat{U}(k)$ which has the shape of two diagonal streaks emanating from the origin, the length of each streak being $\sim 1/\xi$, and the width $\sim 1/L$. In addition to the variation in diffuse scattering with $|Q|$ discussed earlier, there is also a marked variation with the orientation of $Q$, as demonstrated in Figure 7.1. The product $Q \cdot U_q$ in Eq.(7.3) will cause diffuse scattering resulting from $U_+$ to vanish for $Q \parallel (1, 1)$ and the diffuse scattering from $U_-$ to vanish for $Q \parallel (1, -1)$. (See Figure 7.1.) This is known as the "extinction condition" associated with $\{110\}/(1\overline{1}0)$ shears.

In theory, then, longitudinal and transverse correlation lengths of the tweed deformation, $L$ and $\xi$, can be directly extracted from the diffraction pattern. This is precisely the information desired: as pointed out above, experiment has long confirmed the qualitative nature of tweed to be $\{110\}/(1\overline{1}0)$ shears with long diagonal and short axial correlations. A good characterization of the tweedy lattice distortion observed in a particular sample under specified conditions amounts to determining the correlation lengths $L$ and $\xi$. For example, given a series of diffraction data for a sample material as it is cooled from the austenite phase, through the tweed regime, into the martensite phase, it should be possible to quantitatively trace and characterize the development of the tweed deformation in terms of the correlation lengths $L$ and $d$.

Developing a systematic means for extracting lengths scales proved more difficult than anticipated, as the most natural approach fails for subtle reasons. Typically the correlation length is equated with the second moment of a correlation function, a quantity which is easily extracted by measuring the curvature at the origin of the Fourier transformed correlation function. However, in addition to the practical difficulty of measuring the curvature of a trace of the diffuse scattering intensity around a Bragg peak, there is also a much more profound
obstacle, as follows. We have made a point of emphasizing the importance of strain–strain interaction in determining the tweed structure, and in particular, their long range nature as discussed in Chapter 8. These far-reaching interactions naturally lead to an extended correlation function, for which there is no guarantee that the second moment is a convergent quantity. Correspondingly, our simulated diffraction patterns do indeed appear to have a curvature in the diffuse scattering (with the Bragg intensity subtracted off) which diverges, i.e. it is only limited by the simulated system size and will appear as a cusp in the thermodynamic limit. We look forward to acquiring experimental diffraction data which is reliable close enough to the Bragg peak to determine whether this predicted divergence is indeed seen in diffraction from real tweed samples. As discussed in Chapter 5, the suspected long-range correlations in tweed are suggestive of a structure far more cooperative and subtle than mere response to isolated defects or localized pretransitional fluctuations.

We have therefore been confounded in our attempts to independently deduce the real space correlation length from the corresponding diffraction trace. Despite this unanticipated difficulty, there is still information to be salvaged from these uncooperative diffraction data. The nature of the tweed regime, as an intermediate phase between two others, suggests that we consider the evolution of tweed as an external parameter is varied. We have found ourselves unable to deduce the desired information from a single diffraction pattern, but we can compare across a range of diffraction patterns corresponding to tweed observed over a range of some variable parameter, such as temperature, nominal composition, external pressure etc. For example, a particularly interesting prospect is to determine the behavior of tweed as the onset of martensitic nu-
cleation occurs, which would potentially yield valuable information relating the presence of tweed to the creation of martensitic domains.

The most straightforward means of extracting a lengthscale from a graph such as a diffraction pattern or correlation function is to simply read off a measurement such as a full width at half maximum. Within the study of critical phenomena, where scale invariance and universality are fundamental concepts employed in the analysis of measured data, the simple notion of a full width at half max is dignified by the process of scaling collapses. For a range of external parameters, the tweed deformation will not differ qualitatively, but will simply be characterized by a variation in the correlations lengths \( L \) and \( \xi \). Our approach in analyzing the tweed corresponding to a series of diffraction patterns is to collapse them by scaling the inverse–length axis. By collapsing all the diffraction traces onto a given reference pattern, the relative correlation lengths, (although not the absolute correlation length) can be deduced. Figure 7.3 shows the uncollapsed and collapsed diffraction traces for the (110) and (110) traces around the (220) Bragg peak. Because it is particularly apropos to this model of disorder–driven tweed, we have varied as the control parameter the strength of the coupling to compositional variation, \( A_\eta \). From these we can follow the development of the tweed structure by plotting the collapse scaling factor against \( A_\eta \).

As a check on this method of comparing tweed configurations by collapsing diffraction traces, we return to real space and confirm that the scaling factors we’ve calculated are reasonably confirmed by the analogous real space correlation functions. Figure 7.4 shows the collapsed and uncollapsed correlation functions along the \( L \) and \( \xi \) directions. Perfect matching between the real space and \( k \)-space collapses would imply that the two scaling factors should be
Figure 7.3  Uncollapsed and collapsed diffraction traces along the (11) and (10) directions.
inversely related. Figure 7.5 shows the reasonable agreement between the two sets of collapses, particularly for configurations where finite size effects are not yet important. The scaling factors for the real and $k$-space images tend to fall within a factor of two in either direction.

Some subtleties arise in the process of collapsing the correlation functions. First, the real space correlation function conflates the independent effects of the $U_+$ and $U_-$ components of the displacement field. In $k$-space, we benefit from the extinction condition which chooses one component of the displacement field and removes the other. Computationally, this problem is trivially managed by resolving the displacement field into a component along each of the two diagonal directions and calculating the correlation function independently. Figure 7.6 shows the real space configuration corresponding to the $U_-$ component of the displacement field shown in Figure 7.7b - a pattern remarkably similar to TEM images formed by selecting one set of Bragg peaks from which to reconstruct the real space image. (See Figure 3.1)

The second difficulty arises from the fact that we are studying a phase near the onset of long-range martensitic order. In magnetic systems, for example, the correlation function is meaningful only after subtracting off the mean magnetization: correlation fluctuations are the meaningful physical quantity. In our martensitic system, long-range order consists of homogeneous martensitic shear developing over macroscopic volume of material, just as finite magnetization is established in the ferromagnetic phase of magnetic systems. Although we maintain that no long-range (spatial) order exists in tweed, large fluctuations become important finite size effects in our simulations. As a result, the long diagonal correlation length $L$ will lead to finite mean displacements $U_0$ of all the sites along a diagonal. This effect can be accounted for by subtracting
Figure 7.4  Uncollapsed and collapsed real-space correlation functions along the $(11)$ and $(10)$ directions. The large spurious positive correlation at long distances in the $(10)$ directions is a finite size effect that naturally results from the periodic boundary conditions: a given diagonal will be reproduced periodically at intervals of $N/2$. There will of course also be additional translation of $N/2$ parallel to the diagonal, causing the spurious correlation to decrease as $L$ decreases.
Figure 7.6 The displacement field $U(x, y)$ projected onto the $(11)$ direction, yielding $U_-(x - y)$. 
off the resulting spurious additive constant $U_6^2$ from the contribution of each diagonal to the correlation function. Another way to account for these non-zero mean displacements would be to instead calculate a $\phi-\phi$ correlation function, which would be less sensitive to long wavelength modes. The $\phi-\phi$ correlations, however, are not quite so immediately related to the diffraction intensity as the displacement-displacement correlations.

Finally, we plot the correlation lengths as extracted from the real space configurations in Figure 7.8. The rough dimensional arguments sketched in Appendix B suggest that the length scales should vary with the coupling strength as $L \sim A^4_\eta$ and $\xi \sim A^{-2}_\eta$, (everything else being equal). While finite size effects appear to be affecting $L$ for systems at small disorder and lattice effects clearly are affecting $\xi$ at large disorder, the dependence on $A_\eta$ does not appear as strong as that predicted. Measurements on larger systems would be necessary to definitely test this prediction.
Figure 7.8  Correlation Lengths along (11) and (10) plotted vs. strength of the coupling to composition, $A_\eta$. 
Chapter 8
Compatibility and Non-Local Interactions

We wish to repeatedly emphasize that an essential aspect of the physics underly-
ing tweed is that any local fluctuation in the elastic free energy functional (e.g., due to compositional inhomogeneity) cannot be regarded in isolation. The lattice response is not simply a superposition of the responses expected for indepen-
dently considered sites of disorder. Rather, mutual non-local interactions be-
tween spatially separated regions conspire to give an extended cooperative re-
ponse: i.e. the tweed phenomenon. In this chapter we develop a simple yet illuminating analysis which explicitly uncovers the effective non-local in-
teraction which leads to these extended cooperative responses. We write the non-local interaction in terms of a renormalized Fourier space elastic constant, and show that the specific form of the tweed deformation immediately follows.

The only explicit non-local effect is the strain gradient term $(\nabla \phi)^2$ in the free energy

$$F = \frac{A_1}{2} e_1^2 + \frac{A_2}{2} e_2^2 + A_3 \phi^2 - \frac{B}{4} \phi^4 + \frac{C}{6} \phi^6 + \kappa (\nabla \phi)^2$$  \hspace{1cm} (8.1)

However, even disregarding this term, the order parameter $\phi$ cannot be an en-
tirely arbitrary function of position: there is no guarantee that such a field (even if continuous) is physical. This problem relates to the following im-
portant subtlety of any Landau-Ginzburg-type model which treats elastic strain as the relevant order parameter: the true degrees of freedom in a continuum elastic medium are contained in the displacement field, $U(x)$, even though it is the strain fields, $e_{ij}$, which appear in the free energy. Instead of treating the strains as independent fields, one must assure that they correspond to a
physical displacement field, i.e. that they are derivatives of a single continuous function. This is done by requiring that they satisfy a set of non-trivial *compatibility relations* \(^{87}\) concisely expressed by the equation\(^{122}\) \(\nabla \times (\nabla \times \mathbf{e}) = 0\). In two dimensions expands to yield

\[
\nabla^2 e_1 - \sqrt{8} \partial_{xy} e_2 - (\partial_{xx} - \partial_{yy}) \phi = 0.
\]  

(8.2)

Ignoring this geometrical compatibility constraint and minimizing the free energy directly would lead to the incorrect result that \(e_1\) and \(e_2\) are identically zero, and \(\phi\) (the only field directly coupled to the composition) trivially responds to the local disorder. We can explicitly account for the compatibility constraint\(^{\dagger}\) by appending it to the free energy (8.1) via a Lagrange multiplier, \(\lambda(x)\). It is then possible to solve for \(e_1\) and \(e_2\) because we have two constraints relating the three strain fields: the compatibility condition (8.2) and the requirement that the free energy (8.1) is minimized. Solving for \(e_1\) and \(e_2\) in terms of the order parameter \(\phi\), we are able to express the free energy in terms of \(\phi\) alone. The contributions of \(e_1\) and \(e_2\) to the free energy will be accounted for by terms which have the appearance of a non-local interaction coupling \(\phi(x)\) and \(\phi(x')\). Note, by integrating out \(e_1\) and \(e_2\) from the free energy in this way, we are not resorting to an approximation of infinite anisotropy, we are simply analytically solving for the fields \(e_1\) and \(e_2\) in terms of an arbitrary \(\phi\) field.

Proceeding, we find the solutions of the two secondary strain fields \(e_1\) and \(e_2\) which minimize the free energy for a given field \(\phi\) subject to the compatibility constraint. In the standard way, we extremize the free energy with respect to

\(^{\dagger}\) Note: the computer simulation uses the displacement fields as the degrees of freedom, so this geometric compatibility is automatically guaranteed; it is taken into account implicitly because the simulation algorithm considers distortions of a defect-free lattice.
variations in the strain fields, and find Euler-Lagrange "equations of motion" relating the two secondary strain fields to $\phi$. Introducing variations $\delta e_1$, $\delta e_2$, and $\delta \lambda$ into (8.1) yields

$$\delta f = A_1 e_1 \delta e_1 + A_2 e_2 \delta e_2 + \lambda \left\{ \nabla^2 \delta e_1 - \sqrt{8} \frac{\partial}{\partial x} \delta e_2 \right\}$$

$$+ \delta \lambda \left\{ \nabla^2 e_1 - \sqrt{8} \frac{\partial}{\partial x} e_2 - \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) \phi \right\}$$

(8.3)

Doing the requisite integrations by parts, and requiring that $\delta f$ is zero, we find the following Euler–Lagrange equations of motion:

$$e_1 = \frac{-1}{A_1} (\nabla^2 \lambda) \quad (8.4a)$$

$$e_2 = \frac{\sqrt{8}}{A_2} \left( \frac{\partial}{\partial x} \lambda \right) \quad (8.4b)$$

where $\lambda$ is given by:

$$\frac{-1}{A_1} (\nabla^2)(\nabla^2 \lambda) - \frac{8}{A_2} \left( \frac{\partial}{\partial x} \lambda \right) = \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) \phi$$

(8.4c)

This opaque set of equations becomes quite transparent after reexpressing in k-space in terms of $\tilde{\phi}(k)$:

$$\tilde{\lambda}(k) = \frac{(k_x^2 - k_y^2)}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_1} \, \tilde{\phi}(k) \quad (8.5a)$$

$$\tilde{e}_1(k) = \frac{(k_x^2 + k_y^2)(k_x^2 - k_y^2)/A_1}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2} \, \tilde{\phi}(k) \quad (8.5b)$$

$$\tilde{e}_2(k) = \frac{-\sqrt{8}(k_x k_y)(k_x^2 - k_y^2)/A_2}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2} \, \tilde{\phi}(k) \quad (8.5c)$$

The free energy, which is now a functional of $\phi$ alone, now may be expressed
\[ F = \iint dr\, dr' \, f_1(r, r') \, \phi(r) \, \phi(r') + \iint dr\, dr' \, f_2(r, r') \, \phi(r) \, \phi(r') \]

\[ + \int f_{\text{local}}(\phi(r))\, dr \]  

(8.6)

where \( f_{\text{local}} \) is the part of the free energy (8.1) which is explicitly dependent on \( \phi \) alone. The non-local interactions \( f_1 \) and \( f_2 \) account for the free energy contribution due to the \( e_1 \) and \( e_2 \) strain fields, respectively. They are given by

\[ f_1(r, r') = \int \frac{dk}{a} \frac{A_1}{2} \left[ \frac{(k_x^2 + k_y^2)(k_x^2 - k_y^2)}{8(k_x^2 k_y^2)/A_2 + (k_x^2 + k_y^2)^2/A_1} \right]^2 e^{i\mathbf{k} \cdot (r-r')} \]  

(8.7a)

and

\[ f_2(r, r') = \int \frac{dk}{a} \frac{A_2}{2} \left[ \frac{\sqrt{8}(k_x k_y)(k_x^2 - k_y^2)}{8(k_x^2 k_y^2)/A_2 + (k_x^2 + k_y^2)^2/A_1} \right]^2 e^{i\mathbf{k} \cdot (r-r')} \]  

(8.7b)

where \( a \) is the system area. More transparently, we can write

\[ F_1 = \int \frac{dk}{a} \frac{A_1}{2} \left[ \frac{(k_x^2 + k_y^2)(k_x^2 - k_y^2)}{8(k_x^2 k_y^2)/A_2 + (k_x^2 + k_y^2)^2/A_1} \right]^2 |\phi(k)|^2 \]  

(8.7a)

and

\[ F_2 = \int \frac{dk}{a} \frac{A_2}{2} \left[ \frac{\sqrt{8}(k_x k_y)(k_x^2 - k_y^2)}{8(k_x^2 k_y^2)/A_2 + (k_x^2 + k_y^2)^2/A_1} \right]^2 |\phi(k)|^2 \]  

(8.7b)

These terms are thus simple harmonic terms, where the bare elastic constants \( A_1 \) and \( A_2 \) are now \( k \)-dependent. The harmonic term in \( \phi \) is now

\[ \int \frac{dk}{a} \frac{A_\phi(k)}{2} |\phi(k)|^2 \]  

(8.8)

with the restoring force \( A_\phi(k) \) given by

\[ A_\phi(k) = A_\phi + A_1 \, Q_1(k)^2 + A_2 \, Q_2(k)^2 \]  

(8.9)

where

\[ Q_1(k) \equiv \frac{(k_x^2 + k_y^2)(k_x^2 - k_y^2)/A_1}{8(k_x^2 k_y^2)/A_2 + (k_x^2 + k_y^2)^2/A_1} \]  

(8.10)
and

\[ Q_2(k) = \frac{\sqrt{8}(k_xk_y)(k_x^2 - k_y^2)/A_2}{8(k_x^2k_y^2)/A_2 + (k_x^2 + k_y^2)^2/A_1}. \]  

(8.11)

The key feature of this non-local interaction is the factor \((k_x^2 - k_y^2)\), which leads in a natural way to a tweedy deformation, as follows.

In Chapter 5, we showed that in the approximation of infinite elastic anisotropy (in which the elastic constants \(A_1\) and \(A_2\) are assumed to be infinite and only \(A_\phi\) remains finite) the order parameter field must be a sum of one dimensional modulations with tweedy diagonal correlations. The analysis of the current chapter allows us to generalize these infinite anisotropy results to the case of finite anisotropy. One can immediately see from Eq. (8.5b) and Eq. (8.5c) that strains \(e_1\) and \(e_2\) will be generated by non-zero \(\phi(k)\), except for Fourier components for which \(k_x^2 - k_y^2 = 0\). Equivalently, one can see from (8.7a) and (8.7b) that only Fourier components of \(\phi(k)\) with \(k_x^2 - k_y^2 = 0\) will incur no free energy cost through the terms \(f_1\) and \(f_2\), and that their contributions to the harmonic restoring force (8.9) go to zero. As a result, even for finite elastic anisotropy, non-diagonal Fourier components of \(\phi\) with \(k_x^2 - k_y^2 \neq 0\) will be suppressed relative to diagonal components, which will be increasingly prominent for increasing anisotropy. The resulting deformation is a tweedy modulation with long but finite diagonal correlations.

The significance of this nonlocal interaction lies partly in the anisotropy of the interaction, as explained above, but also in the range of the interaction. In Figure 8.2, we plot the numerically integrated function \((f_1 + f_2)\) along the axial and diagonal directions. The interaction strength along the axial directions is positive, strongly suppressing axial correlations. The interaction along the diagonal direction is negative, enhancing diagonal correlations but only insofar
Figure 8.1 Summing the two interactions $f_1(r, r')$ and $f_2(r, r')$, and using materials parameters for FePd as in the simulation, gives us the full form for the nonlocal interaction $f(r - r')$ relating $\phi(r)$ and $\phi(r')$. (The function is truncated near the origin to maintain a reasonable scale.)
Figure 8.2 \( f(0, r) \) is plotted along the diagonal (open circles) and axial (closed circle) directions. Note the \( 1/|r|^2 \) dependence of the interaction strength in the large \( r \) limit. Distance is in units of lattice constants, and the y-axis is in arbitrary units.
as this interaction survives the $k_x^2 - k_y^2$ suppression. (Note, here we plot in Figure 8.2 the negative of the interaction strength along the diagonal direction for better comparison). As one can see from the figure, this long-range interaction dies off like $1/r^2$, and will produce logarithmic divergences in a two dimensional system. The inevitable result is the development of extended, coordinated lattice modulations which take advantage of the compositional disorder without generating unnecessary strains: i.e. tweed.
Chapter 9

Alternative Couplings

A central premise of this research is that compositional disorder can no longer be ignored, and must be considered when studying a mesoscale phenomenon such as tweed. We have chosen a particular way to include this disorder in our model, and in this chapter we would like to further discuss the significance of that choice and investigate the possible alternatives.

As first discussed in Chapter 3, the importance of compositional disorder is quite vividly evidenced by the drastic dependence of the transformation temperature on composition: composition is unquestionably coupled to the martensitic transformation. In Chapter 4 and Appendix A we noted that the simplest coupling between the martensitic strain $\phi$ and the composition $\eta$ is $\eta\phi^2$, and this term was therefore included in our Landau free energy. True, this term is the simplest coupling between a scalar field and the order parameter $\phi$. However, our decision to consider a scalar field coupled directly to the $\phi$ component of the strain field requires justification, since non-scalar disorder fields and the other strain components can not in principle be neglected out of hand.

First, we've chosen to couple to $\phi$ directly for the same reason that we've taken it as our order parameter and included its anharmonic terms: $\phi$ is the predominant strain measured in the tweed deformation and it is the strain responsible for the martensitic transformation. As such, it is larger in magnitude than the other strain components and will be most susceptible to interacting with some driving force, whether due to intrinsic disorder or some extrinsic field such as an externally applied stress.
Second, we've chosen a scalar disorder field simply because tweed is so impressively widespread a phenomena, and we desire to study the simplest, most universal disorder. Indeed, there are important materials with unit cell configurations that allow for some disorder field more complicated than simply scalar: the obvious example is oxygen distribution in YBCO. However, we find it provocative that tweed appears in materials with even simple lattices such as FCC or BCC. Here, disorder takes the form of random placement of atoms, with each site being symmetrically equivalent with every other. In this case, disorder is necessarily simply a scalar field for which the square symmetry precludes a linear coupling. Even in the case of nickel-rich Ni_xAl_1-x, which has an ordered β-CsCl structure, the compositional disorder can be described by a scalar field corresponding to the positions of the excess nickel atoms, which are accommodated by random substitution onto the aluminum sublattice.^1^2^3^.

Third, we know that composition couples not only to the martensitic transformation strain, but to the martensitic transformation temperature. Compositional inhomogeneities will result in a spatially varying transformation temperature, and in a \( \phi^6 \) Landau free energy this is reflected in spatial variations in the coefficient of \( \phi^2 \).

Fourth, the experimental observation of hysteresis immediately allows us to conclude that a simple linear response mechanism cannot be the general origin of tweed. Hysteresis is seen^6^1^ to occur upon cycling of temperature: upon heating, the tweed pattern persists up to a temperature which is higher than that at which it initially appeared upon cooling. This hysteresis implies that the tweed is something more complex than simply linear response of the lattice to some static defect or impurity. In linear response, the lattice displacements are calculated as a single-valued function of the perturbing force, and the tweed
would therefore form and fade without history dependence. The temperature
dependence of the tweed pattern would arise from the (single-valued) temper-
ature dependence of the elastic constants, and it is difficult to conceive of a
possible source of hysteresis in this mechanism.

Still, despite the above justification for the $\eta \phi^2$ coupling, in this chapter we
will round out our study of the origin of tweed by investigating other symmetry-
allowed couplings.

9.1 Coupling to Order Parameter Linearly:

The system in which tweed has received the greatest amount of attention in
the last several years is the high temperature superconductors. In the YBCO
type materials, there are twice as many oxygen sites in the Cu-O planes as
oxygen atoms, and the tetragonal to orthorhombic martensitic transition oc-
curs as the randomly distributed oxygen atoms break the twofold symmetry
between sites and preferentially align along one axis. This alignment results in
an increased lattice constant in one direction relative to the other, and a net
rectangular deformation in the Cu-O plane. In this case, if the oxygen distri-
bution is taken as the disorder field, disorder clearly couples directly to $\phi$, and
the corresponding term in a Landau free energy describing this system would
appear as a term linear in disorder and strain, $\eta \phi$.

This model has been extensively studied. Khachaturyan et al.$^{68}$ and Parlin-
ski et al.$^{103}$ have each considered a model for YBCO in which diffusing oxygen
atoms arrange into martensitic microdomains, and the coupling between oxy-
gen position and elastic strain leads directly to an unquestionably tweedy lattice
deformation. Morphologically, the tweed structures found in these studies is es-
sentially identical to that presented in this thesis; not only is the qualitative
appearance identical, but quantitatively the correlation lengths are comparable as well. However, there is a fundamental difference in the physical nature of the tweed structures. In their investigations, the tweed is a not an equilibrium phase, but rather a non-equilibrium or metastable configuration. Khachaturyan et al. find that tweed is formed as a transient structure as the oxygen distribution gradually evolves through an ordering process, passing through a stage of highly anisotropic microdomains before reaching the equilibrium twinned martensitic configuration. In addition to this transient tweed, Parlinski et al. also find "embryonic" tweed resulting from thermal fluctuations above the transition temperature, which they treat as critical fluctuations in a second order transition. These studies have produced a dynamic, fluctuating tweed in contrast to the static tweed phase which our model seeks to explain. Yet, despite the compelling analogy, it is not accurate to infer they have produced the liquid out of which our glass forms!

The nature of the disorder in their nonequilibrium tweed is fundamentally different from the nature of the disorder in our equilibrium tweed. The distribution of oxygen atoms constitutes their disorder: randomly scattered or clustered into microdomains or ordered into martensitic variants atoms, the oxygen couples to the strain and gives rise to some lattice deformation. Yet, since the oxygen atoms diffuse in response to external parameters; oxygen is not a source of quenched-in disorder. The oxygen is effectively an additional degree of freedom which the system integrates out as it searches for a stable equilibrium. In this light, it is clear why there is no stable, static tweed to be found in these models. In contrast, the model presented in this thesis relies on the presence of intrinsic quenched-in disorder, in the form of static compositional inhomogeneities, in order to stabilize the tweed phase.
Why then, is static tweed seen in YBCO at all? Significantly, it is when YBCO is doped with an impurity that static tweed appears. After substituting copper with as little as 1.5% of a transition metal element (such as Fe, Co, Al, or Ga), TEM observations of tweed are made. These impurity atoms are frozen in at temperatures well above the tweed regime, typically at \( > 700 \text{K} \), and therefore the impurity disorder is truly quenched-in. It is through the oxygen atoms, which interact differently with the copper atoms than with the impurity atoms, that the static disorder is communicated to the elastic deformation. Studies by Jiang et al.\(^7\) and Krekels et al.\(^5\) have demonstrated microdomain formation due to static impurity atoms. In these studies, the oxygen–copper and oxygen–impurity interactions are such that the impurity atoms prefers nearest-neighbor oxygen occupancy, while the surrounding matrix prefers oxygen chain alignment. Correspondingly, if the elastic strain were taken into account in such models, the impurity atoms would act as sites favoring the square phase amid copper sites favoring the rectangular phase. The compositional variation therefore selects a phase (square or rectangular) but it does not select a particular martensitic variant: the symmetry of copper site within the unit cell prevents it from coupling linearly to the rectangular strain. It is just this physical situation which is represented in our model by a quadratic coupling between compositional disorder \( \eta \) and rectangular strain \( \phi \).

**9.2 Coupling to Gradients of Disorder:**

Although the disorder on an atomic scale can be described by a scalar field, it is possible for the random compositional variations to conspire to produce clusters of more complex symmetry, which may then collectively couple to the order parameter. For example, as Robertson and Wayman\(^5\) have argued with
respect to NiAl, random clusters of nickel atoms have a high probability of having tetragonal symmetry, and therefore coupling to the martensitic strain. In the language of the Landau-Ginzburg formalism, this corresponds to a coupling between higher order gradients of the disorder field and the order parameter. In this section, we consider such terms in both two and three dimensions.

In two dimensions, the term $\phi(\partial_x^2 - \partial_y^2)\eta$ (see Appendix A) is a symmetry-allowed coupling between $\eta$ and $\phi$ which is a priori no less important than the quadratic coupling we have used. Since this term is only linear in $\phi$, it could well be comparable in magnitude to the quadratic coupling, despite the second derivative, and be just as effective in generating some lattice deformation. The relevant question, however, is: what is the capacity of such a term to generate tweed. This is most easily answered by reexpressing the term in k-space: $\tilde{\phi}(k)(k_x^2 - k_y^2)\tilde{\eta}(k)$. Recall that tweed is correlated along diagonal directions, (see Chapter 5 and Chapter 8) and therefore is composed of fourier components for which $k_x^2 - k_y^2 \rightarrow 0$. Therefore, although $(\partial_x^2 - \partial_y^2)\eta$ couples to the order parameter, it does not do so in a manner which allows it to generate tweed.

In three dimensions, the term

$$(9.1)$$

(see Appendix A) is allowed by symmetry. However, integrating by parts and inserting the three dimensional constrained displacement, Eq. (5.18), we get

$$(\partial_x^2 \tilde{\phi}_x) \cdot (\partial_y^2 \tilde{\phi}_y) \cdot (\partial_z^2 \tilde{\phi}_z) = \eta \left( \begin{array}{c} \partial_x^2 \\ \partial_y^2 \\ \partial_z^2 \\ \end{array} \right) \cdot \left( \begin{array}{c} -T' - T'' + U' + U'' \\ S' + S'' - U' - U'' \\ -S' - S'' + T' + T'' \\ \end{array} \right)$$

$$= \eta \left( -T''' - T'' + U''' + U'' + (S''' + S'' - U''' - U''') + (-S''' + S'''' + T''' + T''') \right) = 0.$$ (9.2)
Again, we see any modulation composed of $(110)/(1\bar{1}0)$ shears is unable to couple to the appropriate gradient term. This term will be able to couple a deformation to disorder only to the extent that the deformation is different from that which experimental observations suggests are tweedy.

9.3 Coupling to Bulk Dilation:

Perhaps the most commonly considered deformation due to compositional disorder is that which arises from atomic size mismatch in alloys. This mechanism is represented by the coupling $\eta \varepsilon_1$ between composition and bulk dilation (see Appendix A), and although it does not directly couple $\eta$ and $\phi$, we have repeatedly emphasized that the strain fields are not independent and are intrinsically coupled by the compatibility conditions (see Chapter 8).

In Chapter 8, we were able to translate the bulk dilatation and diagonal strain contributions to the free energy into non-local interactions in $\phi$, by integrating those secondary strains out of the free energy, subject to the compatibility constraint. We can carry out the analogous analysis for a term $D\eta \varepsilon_1$, as follows:

The variation in the free energy caused by variations $\delta \varepsilon_1$, $\delta \varepsilon_2$, and $\delta \lambda$ is

$$
\delta f = (A_1 \varepsilon_1 + D\eta) \delta \varepsilon_1 + A_2 \varepsilon_2 \delta \varepsilon_2 + \lambda \left\{ \nabla^2 \delta \varepsilon_1 - \sqrt{8} \partial_{xy} \delta \varepsilon_2 \right\} \\
+ \delta \lambda \left\{ \nabla^2 \varepsilon_1 - \sqrt{8} \partial_{xy} \varepsilon_2 - \left( \partial_{xx} - \partial_{yy} \right) \phi \right\}
$$

(9.3)

and the corresponding expressions for $\varepsilon_1$, $\varepsilon_2$, and $\lambda$ are

$$
\varepsilon_1 = \frac{-1}{A_1} (\nabla^2 \lambda - D\eta)
$$

(9.4a)

$$
\varepsilon_2 = \frac{\sqrt{8}}{A_2} (\partial_{xy} \lambda)
$$

(9.4b)
\[
- \frac{1}{A_1} (\nabla^2)(\nabla^2 \lambda + D\eta) - \frac{8}{A_2} \left( \partial_{xx} \chi \right) = \left( \partial_{xx} - \partial_{yy} \right) \phi. \quad (9.4c)
\]

In k-space this gives us
\[
\tilde{\lambda}(k) = \frac{(k_x^2 - k_y^2)\tilde{\phi}(k) + (k_x^2 + k_y^2)D\tilde{\eta}(k)/A_1}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_1} \quad (9.5a)
\]
\[
\tilde{\epsilon}_1(k) = \frac{(k_x^2 + k_y^2)(k_x^2 - k_y^2)\tilde{\phi}(k)/A_1 - (k_x^2 k_y^2)D\tilde{\eta}(k)/A_1 A_2}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2} \quad (9.5b)
\]
\[
\tilde{\epsilon}_2(k) = \frac{-\sqrt{8}(k_x k_y)(k_x^2 - k_y^2)\tilde{\phi}(k)/A_2 - (k_x k_y)(k_x^2 + k_y^2)D\tilde{\eta}(k)/A_1 A_2}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2} \quad (9.5c)
\]

Again, the free energy can now be written in terms of \( \phi \) alone. The contributions due to \( A_1 \epsilon_1^2 \) and \( A_2 \epsilon_1^2 \) are identical to those found in Chapter 8, as they must be, with the terms proportional to \( \tilde{\eta} \) canceling. The contribution from the disorder term, \( D\eta \epsilon_1 \) is now a non-local interaction between disorder and \( \phi \) (where the term quadratic in disorder can be dropped by redefining the zero of the energy):
\[
F_\eta = \int \int d\mathbf{r} \, d\mathbf{r}' \, f_\eta(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}) \eta(\mathbf{r}') \quad (9.6)
\]
where
\[
f_\eta = \int \frac{d\mathbf{k}}{a} \frac{D}{A_1 (k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \quad (9.7)
\]

More transparently, we can write
\[
F_\eta = \int \frac{d\mathbf{k}}{a} \frac{D}{A_1 (k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2} \tilde{\phi}(\mathbf{k}) \tilde{\eta}(-\mathbf{k}) \quad (9.8)
\]

In the previous section we casually argued that a term like this one will be ineffective in generating a tweedy deformation because it vanishes precisely for those Fourier modes \( (k_x \simeq \pm k_y) \) which correspond to tweed. A more careful analysis would account for the fact that the restoring force \( A_\phi(\mathbf{k}) \) is \( k \)-dependent, and diminishes as \( k_x \pm k_y \to 0 \), reinforcing the effectiveness of this
driving force. The term in the last section turns out to indeed be harmless, but here we give a more complete analysis. Within linear elasticity, it is possible to solve explicitly for the deformation resulting from Eqs. (9.8).

We are considering the harmonic free energy

$$F = \int \frac{d\mathbf{k}}{a} \frac{A_\phi(k)}{2} |\phi(k)|^2 + D Q_1(k) \tilde{\phi}(k) \tilde{\eta}(-k)$$

(9.9)

where $A_\phi(k)$ and $Q_1(k)$ defined in Eqs. (8.9) and (8.10) respectively. This is minimized when

$$\tilde{\phi}(k) = -\frac{D Q_1(k) \tilde{\eta}(-k)}{A_\phi(k)}.$$  

(9.10)

The most revealing measure of this simple result is the corresponding diffraction pattern for a white disorder distribution $\eta(k) = \eta$, which we calculate using

$$\left( \begin{array}{c} \tilde{\phi}(k) \\ \sqrt{2} \tilde{\epsilon}_2(k) \end{array} \right) = \frac{1}{\sqrt{2}} \begin{pmatrix} k_x & -k_y \\ k_y & k_x \end{pmatrix} \begin{pmatrix} U_x(k) \\ U_y(k) \end{pmatrix}$$

(9.11b)

and

$$\tilde{\epsilon}_2(k) = -Q_2(k)\tilde{\phi}(k) - \frac{D\eta}{A_1} Q_3(k)$$

(9.12)

where

$$Q_3(k) = \frac{(k_x k_y)(k_x^2 + k_y^2)/A_2}{(k_x^2 + k_y^2)^2/A_1 + 8(k_x^2 k_y^2)/A_2}.$$  

(9.13)

We can invert Eqs. (9.11) and use Eqs. (9.10) and (9.12) to find

$$\begin{pmatrix} U_x(k) \\ U_y(k) \end{pmatrix} = \frac{\sqrt{2}}{k^2} \begin{pmatrix} k_x & k_y \\ -k_y & k_x \end{pmatrix} \begin{pmatrix} -\frac{D\eta Q_1(k)}{A_\phi(k)} \\ \sqrt{2} \left\{ \frac{D\eta Q_1(k) Q_2(k)}{A_\phi(k)} - \frac{D\eta}{A_1} Q_3(k) \right\} \end{pmatrix}$$

(9.14)

The scattering contours in Figure 9.1 were calculated from the solution (9.14) to the linear problem. For finite anisotropy, the diffuse scattering deviates substantially from that expected from tweed, showing that a substantial amount of non–tweedy deformation is occurring in the lattice. This is in agreement with
Figure 9.1  Diffraction contour around Bragg peaks (04), (24) and (22) (from left to right) at anisotropies $A = 1$, $A = 5$, and $A = 50$ (from top to bottom.) The coupling strength $D$ was scaled with the anisotropy, so that the net deformation is constant in magnitude, but increasingly tweedy. Since tweed can be observed in FePd, for example, when the anisotropy is as small as $A = 5$, this implies that tweed cannot be explained by a linear response to a coupling to bulk dilation.
the much earlier analysis of Cochran and Kartha\textsuperscript{124} who show that the long-range strain field associated with random variation in bulk dilation will lead to diffuse scattering with a strong radial component at \(\langle 0h \rangle\) Bragg peaks. This is qualitatively distinct from the diagonal diffuse streaking seen in tweed. As the anisotropy increases however, the diffuse scattering lobes converge toward the diagonal directions, and grow increasingly similar to the diagonal streaks associated with tweed.

This suggests that within linear elasticity a coupling \(\eta e_1\) between disorder and bulk dilation is ineffective at generating tweed for most realistic materials parameters. As a more fair test of this coupling, we must also determine whether tweed might still appear in the full non-linear model that includes terms anharmonic in the \(\phi\) strain. Of course, an analytical solution is now unfortunately inaccessible, but introducing the coupling to bulk dilation into our numerical simulation with finite anisotropy, we’ve determined that this coupling does not result in a identifiably tweedy modulation. The configuration in Figure 9.2 was obtained by eliminating the coupling \(\eta \phi^2\) and replacing it with a coupling \(\eta e_1\) of the same strength. The lattice is noticeably deformed, yet the modulations clearly do not constitute tweed.
Figure 9.2  The configuration resulting from a linear coupling to bulk shows no identifiably tweedy modulation.
Chapter 10

Conclusion

This research constitutes a (hopefully not foolish) attempt to pick up the gauntlet laid down by Olson, Tzuzaki, and Cohen in the opening quote of the introductory chapter. We have applied methods well established within the field of condensed matter physics to attack a real world problem which had been largely unstudied by condensed matter physicists: the problem of pretransitional phenomena in first order solid-solid displacive transformations. We've taken the Landau–Ginzburg formalism and adapted it for use as a tool for investigating a "dirty" problem such as tweed. Eventually, this led us (entirely unsuspecting) into the realm of spin glasses, and allowed us to take advantage of an existing perspective on disordered systems, and translate it directly to the materials science question we were studying. The obvious next step is to design a systematic inquiry into the burning question resulting from this research: is tweed a glass?

We have some preliminary ideas about conducting such a study:

There are certain standard measurements which are made in spin glasses in order to verify glassy behavior. The most obvious is to measure the nonlinear magnetic susceptibility at the spin glass transition. We assume that there is a non-linear elastic constant that couples to the Edwards–Anderson order parameter in tweed measuring \( \phi - \phi \) correlations in time, and that this elastic constant would show the appropriate behavior at the transition. The problem is that the transition boundary at which the nonlinear magnetic susceptibility in spin glasses diverges is the spin glass–paramagnetic boundary, whereas the
boundaries analogous to the tweed boundaries are those between the spin glass and the magnetized phases.

If the analogous divergent quantity does not exist, then there are other ways of looking for glassy behavior. Sluggish dynamics may be measured by many different probes, and the analog of the frequency dependent magnetic susceptibility measurements in spin glasses might be found in some of the interesting work which has been done (e.g. Migliori et al.\textsuperscript{44}, Wuttig et al.\textsuperscript{47}, Lee et al.\textsuperscript{46}) on ultrasonic attenuation near the martensite phase boundary. Migliori et al., in particular, have some very intriguing results that strongly suggest that tweed may have dramatic effects on elastic constants. A full frequency dependence measurement is still waiting to be done.

The analog of remanent magnetization is remanent strain. Cooling into the tweed phase and watching for slow relaxation may reveal some very long (logarithmic?) decay times. Speckle interferometry has been suggested to us by Carl Franck and also by Joel Brock as an ideal probe for studying such effects. It offers an extremely precise measurement of very long time-scale behavior.

A possible measurement of the onset of glassy behavior is thermal conductivity. Comparisons have been made (Mitchell and Anderson\textsuperscript{125}) of thermal conductivity between austenite and martensite, but a particularly interesting investigation would measure the change in thermal conductivity near (but still above) the transition, when domain walls don’t appear, and any effect would have to come from a smaller scale (pretransitional?) behavior.

We have been resourceful in conducting our own investigation of glassiness in tweed. Through the same numerical simulation as that presented in Chapter 6, we have investigated the onset of long-range order in time. Lisa Wickham
has established that there is a temperature range over which a dynamic tweed configuration undergoes a transition to a static tweed, where long-time $\phi-$ $\phi$ correlations appear to persist. Despite continued thermalization at a fixed temperature, there seem to be free energy barriers of arbitrarily large size that the system is not able to surmount, typical of a glassy system. Further, we are capable of searching for the predicted remanent strain behavior as another indicator of glassy dynamics.

We have also investigated the softening behavior in the pretransitional tweed regime. We have long suspected that the pretransitional "anomalies" in elastic constant behavior are inextricably connected to the presence of tweed type modulations. Whereas conventional wisdom holds that elastic softening leads to pretransitional modulations (and ultimately to the martensitic transformation), we believe that the softening can in turn be enhanced by the pretransitional modulation. A bulk elastic constant, measured over an entire macroscopic specimen, will necessarily reflect not simply the harmonic response arising from the bare interatomic potentials, but also the mesoscopic lattice response to the applied driving force. When stressed, a modulation such as tweed will certainly respond elastically, but it will also flip domains, depin boundaries, rearrange clusters etc. We believe that it is precisely such nonlinear processes which account for much of the behavior underlying the pretransitional anomalies in elastic softening, internal friction, and acoustic attenuation. We've undertaken to investigate these effects in our model by studying the response of a simulated patch of tweed to an externally applied strain. Allowing these relaxational processes, we measure elastic constants which are substantially softer that the "bare" elastic constants otherwise found. Furthermore, we observe the dissipative and hysteretic effects
which underlie the experimental ultrasonic attenuation and internal friction measurements.

Finally, we would like to note that many of the key ideas which have arisen in this work have also been of central importance in earlier work by a number of other investigators. Ericksen\textsuperscript{126} and Jacobs\textsuperscript{91} have considered the limit of infinite anisotropy and shown the general form for allowed solutions. Khachaturyan and Parlinski et al. have noted the vital importance of the long-range nature of strain fields in a lattice modulation such as transient\textsuperscript{68} and dynamical\textsuperscript{103} tweed. Jiang et al.\textsuperscript{75}, Krekels et al.\textsuperscript{57} and Becquart et al.\textsuperscript{76} have recognized the importance of compositional randomness (i.e. random placement of alloy components or dopants) in determining the tweed structure. We have assembled these various ingredients into a strikingly simple and powerfully general model which provides compelling answers to two questions which have been troubling investigators of pretransitional phenomena in martensitic materials for many years: What is tweed? Why does it occur? Moreover, the answers given here have established an unexpected connection between tweed and spin glasses, suggesting a new line of experimental investigation into tweed. In establishing this connection, it is hoped that the tools being developed within the field of disordered systems in condensed matter theory may be brought to bear on the “dirty” problem of pretransitional phenomena in martensitic systems.
Appendix A
Generating Scalars

Any model which hopes to describe a real system must, at the very least, fulfill the basic requirement that all symmetries of the real system are faithfully respected. In Landau theory, symmetry considerations are paid the utmost respect; symmetry serves as the single guiding principle in constructing the free energy functional which determines a system's behavior. Without resort to any deeper or more constraining physics, the free energy is simply taken as a Taylor expansion in powers of the order parameter and its gradients which is invariant under the symmetry group of the system in question. In this way, Landau theories are used to generate simple, generic models for phenomena so general that they are largely model independent. Since tweed is indeed so commonplace, we happily analyze it in this simple context. In this appendix, we produce the scalars out of which the free energy is composed, for the case of the two dimensional system with square symmetry (point group $C_{4v}$) and the three dimensional cubic system (point group $O_h$).

The approach is as follows. Making use of well-established group theoretical methods, we refer to the character table corresponding to the high symmetry phase for each of the two phase transitions we are considering. Knowing the characters of each of the irreducible representations of the point symmetry group allows us to determine the representational decomposition of direct product spaces composed of products of the order parameter (and its gradients). We produce each term in the free energy by determining the linearly independent scalars contained within a given direct product space. Since a central focus of this thesis research is the influence of compositional disor-
der on the tweed deformation, we must also consider invariants which include the composition field. Obviously, scalars of arbitrarily high order in the order parameter and its gradients exist, but we go only up to the order needed to reproduce the relevant physics, i.e. a first order phase transition, a gradient energy\(^{102}\) to suppress uncontrolled modulation, and a coupling between compositional disorder and the order parameter. This appendix is organized as a case study in constructing a Landau-Ginzburg free energy, with the aim of making explicit the process of applying this very general methodology. We also take this opportunity to bring to the readers attention certain technical subtleties which arise along the way.

**A.1 Two Dimensions: The Point Group \(C_{4\text{v}}\)**

Table A1 below\(^{127}\) gives the characters for the irreducible representations of the \(C_{4\text{v}}\) point symmetry group. The character \(\chi^{\varphi}(G)\) of an object \(\varphi\) is simply the trace of the matrix which transforms \(\varphi\) through symmetry \(G\). The symmetries denoted by the symbols \(E\), \(C_2\), \(2C_4\), \(2\sigma_v\), and \(2\sigma'_v\) are as follows: \(E\) is the identity, \(C_2\) is a rotation through angle \(\pi\) around the fourfold symmetry axis, \(C_4\) is a rotation through angle \(\frac{\pi}{2}\) around the fourfold symmetry axis, \(\sigma_v\) is a reflection about a twofold symmetry axis passing through midpoints of opposite edges, and \(\sigma'_v\) is a reflection about a diagonal.

**A.1.1 Scalars Constructed from \(\phi\):** The order parameter \(\phi\) is a strain, and therefore simply a product of gradients and displacements, both of which are vector objects. Writing down the matrices corresponding to the vector representation will therefore allow us to quickly determine the character of the order parameter. Sample matrices corresponding to one member of each of the five symmetry classes are given below, and it is quickly seen that the traces of
Table A1  The character table for the $C_{4v}$ point symmetry group.

<table>
<thead>
<tr>
<th>$C_{4v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$2C_4$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

these matrices match the expected characters for the irreducible representation E in the point group $C_{4v}$.

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},$$

$$\sigma_v = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma'_v = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (A1)$$

Since the gradient operator $\nabla = (\partial_x, \partial_y)$ and the displacement field $U = (U_x, U_y)$ are both vectors, it is straightforward to write the representation for the object $(\partial_x U_x, \partial_y U_y) = (e_{xx}, e_{yy})$, and from that the representation for the order parameter $\phi = \frac{e_{xx} - e_{yy}}{\sqrt{2}}$. For $(e_{xx}, e_{yy})$,

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},$$

$$\sigma_v = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma'_v = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (A2)$$

and accordingly, for $\phi$

$$E = 1, \quad C_2 = 1, \quad C_4 = -1, \quad \sigma_v = 1, \quad \sigma'_v = -1, \quad (A3)$$

(where a symmetry transformation "matrix" for the one component object $\phi$ is simply a single number.) Finally, we can simply read off the character of our
order parameter: \( \chi^\phi \{ G \} = \{ 1,1,-1,1,-1 \} \). We confirm immediately that the order parameter is an irreducible representation of the symmetry group \( C_{4v} \), and in particular, \( \phi \) transforms as a \( B_1 \)-object.

With this information in hand, we now proceed to calculate the scalars which can be constructed from powers of the order parameter \( \phi \) and the gradient operator \( \nabla \). The character \( \chi^{\alpha\beta}(G) \) for a direct product space \( \alpha \times \beta \) is given by the product of the characters of the two representations,

\[
\chi^{\alpha\beta}(G) = \chi^\alpha(G)\chi^\beta(G),
\]

(A4)

where \( G \) is some member of the point group. In particular, the \( n \)th power of the representation \( \alpha \), (reducible or irreducible) is given simply by

\[
\chi^{\alpha n}(G) = (\chi^\alpha(G))^n
\]

(A5)

This gives us our first result, trivial yet revealing, that powers of \( B_1 \)-objects have the character \( \chi^{\phi n} \{ G \} = \{ 1,1,(-1)^n,1,(-1)^n \} \), which has the immediate corollary that all even powers of \( \phi \) are scalars, i.e. have \( \chi^{\phi 2n} \{ G \} = \{ 1,1,1,1,1 \} \) and are \( A_1 \)-objects. Our free energy can therefore contain any even power of the order parameter.

For completeness, we briefly consider the other strain components. It easily seen from eqs. (A2) that \( e_1 \equiv \frac{e_{xx} + e_{yy}}{\sqrt{2}} \) has \( \chi^{e_{1}} \{ G \} = \{ 1,1,1,1,1 \} \), and therefore \( e_1 \) and all powers \( e_{1}^n \) are scalars, \( (A_1 \)-objects). Similarly, \( e_2 \equiv e_{xy} \) is a \( B_2 \)-object having \( \chi^{e_{2}} \{ G \} = \{ 1,1,-1,-1,1 \} \). Just as for \( \phi \), all even powers of \( e_2 \) are scalars. As explained in Chapter 5, powers higher than \( e_1^2 \) and \( e_2^2 \) (including cross terms) are neglected, as these strains are secondary in importance to the strain order parameter \( \phi \), and their magnitude is much smaller. (At the risk of excessive pedantry, we make two additional points: 1) the only linear scalar.
$e_1$, is excluded from the free energy as required by the condition of mechanical stability, i.e. its coefficient is zero in equilibrium. 2) The antisymmetric term $\omega \equiv e_{xy} - e_{yx}$ has $\chi^\omega \{ G \} = \{ 1, 1, 1, -1, -1 \}$, making it an $A_2$-object, which again is a scalar when raised to even powers. However, as $\omega$ is the rotational part of the strain field, scalars in $\omega$ are excluded from the free energy expression as demanded by rotational invariance.)

**A.1.2 Scalars Constructed from $\nabla$ and $\phi$:** This concludes the search for scalars constructed solely from powers of $\phi$. Now, we have the more involved task of determining scalars constructed from powers of the gradient operator $\nabla = (\partial_x, \partial_y)$ (an $E$-object), and the order parameter $\phi$. The resulting gradient expansion is usually justified by the presumption that the order parameter field of interest varies slowly on the scale of the atomic spacing. For the present system, this presumption may in certain cases be somewhat suspect, as the shortest correlation length $\xi$ in tweed can be on the order of only a few lattice constants. For further discussion, see Ref. 102, 130, 131.

Proceeding in order of increasing powers, we first take terms generated by the direct product of the gradient and the order parameter, denoted $\nabla \times \phi$, which have character $\chi^{\nabla \phi} \{ G \} = \chi^{\nabla} \{ G \} \chi^\phi \{ G \}$. The character is therefore $\chi \{ G \} = \{ 2, -2, 0, 0, 0 \}$, telling us that $\nabla \times \phi$ is simply the irreducible representation $E$. Explicitly, $(\partial_x \phi, \partial_y \phi)$ is simply a vector, and there are no scalars to be extracted at this order.

Before proceeding to higher order in $\nabla$ and $\phi$, a precautionary point must be made. In determining the character of a representation generated by the direct product of two representations, say $\varphi$ and $\psi$, it is often convenient to decompose the direct product space into symmetric and antisymmetric sub-
spaces, corresponding to terms of the form \((\varphi_i \psi_j + \varphi_j \psi_i)\) and \((\varphi_i \psi_j - \varphi_j \psi_i)\), respectively. These subspaces are representations, (not generally irreducible), and their characters can be considered individually. It is easily shown that the character of the symmetric space is given by

\[
\chi_{\text{sym}}(G) = \frac{1}{2} \left\{ \left( \chi^{\varphi \psi}(G) \right)^2 + \chi^{\varphi \psi}(G^2) \right\}
\]  

(A6a)

and the character of the antisymmetric subspace is given by

\[
\chi_{\text{anti}}(G) = \frac{1}{2} \left\{ \left( \chi^{\varphi \psi}(G) \right)^2 - \chi^{\varphi \psi}(G^2) \right\}
\]  

(A6b)

When \(\varphi\) and \(\psi\) are the same, the antisymmetric representation vanishes, since all its basis elements are manifestly zero. (For example, this principle is reflected in the fact that the cross product of a vector with itself vanishes: the antisymmetric subspace of the direct product space \(v \times w\), where \(v\) and \(w\) are three dimensional vectors, is given by the vector \((v_yw_z - v_zw_y, v_zw_x - v_xw_z, v_xw_y - v_yw_x)\), which is obviously zero if \(v = w\).) This might suggest that, for the problem at hand, we need consider only the symmetric subspace of a direct product space such as \(\nabla \times \nabla \ldots \nabla\) or \(\phi \times \phi \ldots \phi\), which can substantially simplify the task of reducing the product representation into irreducible representations. (Generalizations of Eqs. (A6) to arbitrary \(n\) prove helpful here. Expressions for \(n = 3\) and \(n = 4\) are shown below.) However, we caution the reader that it is important to verify that the antisymmetric subspace which is being neglected is indeed a null subspace. In other words, antisymmetric terms of the form \((\varphi_i \varphi_j - \varphi_j \varphi_i)\) tend to be summarily discarded on the grounds that invariance under permutation of indices makes all antisymmetric expressions zero. Indeed, when the objects \(\varphi_i, \varphi_j\), etc. are, say, components of a vector, commutativity trivially applies and indices may be freely permuted, as the above example of \(v \times w\)
demonstrates. Or, when the objects are the operators $\partial_i$, $\partial_j$, etc acting on a given function, again commutivity holds\(^\dagger\), and we obtain $(\partial_i\partial_j - \partial_j\partial_i)f_k = 0$.

However, one must not make general inferences, and invariance under permutation of indices clearly fails in the simple example $\varphi_i\partial_j\varphi_k - \varphi_k\partial_j\varphi_i \neq 0$, since $\varphi_i\partial_j\varphi_k = -\varphi_k\partial_j\varphi_i$ (carrying out one integration by parts and adopting a casual attitude toward surface terms.) Ignoring this term, which resides in the subspace of $\nabla \times \varphi \times \varphi$ which is antisymmetric in $\varphi$, could prove disastrous to any attempt to rigorously generate all classes of scalars. In conclusion, the following warning is issued: one cannot peremptorily discard the antisymmetric subspace of a direct product representation; commutivity and invariance under permutation of indices cannot be assumed.

In light of the preceding warning, we shall search for scalar terms within the entire (symmetric and antisymmetric) direct product space of $\varphi$ and $\nabla$ if problems might arise — a precautionary measure which, as it turns out, costs essentially nothing for the two dimensional problem, and relatively little for the three dimensional problem.

Continuing our search, we consider the next order term in $\varphi$ which is $\nabla \times \varphi \times \varphi$. We can conclude with no calculation whatsoever that this is again a vector representation, since $\varphi^2$ (a scalar) times $\nabla$ (a vector) leaves us a vector, whose character is immediately confirmed to be $\chi^{\nabla \varphi \varphi}\{G\} = \{2, -2, 0, 0, 0\}$.

Considering the product space $\nabla \times \nabla \times \varphi$, we see $\chi^{\nabla \varphi \varphi}\{G\} = \{4, 4, 0, 0, 0\}$ matches none of the irreducible representations of $C_{4v}$. It is therefore reducible, and we would like to know whether it contains the scalar $(A_1)$ irreducible representation. We here use the standard procedure to discover the number $n_r$.

\(^\dagger\) Exceptions can arise – see comments below regarding topological defects.
of irreducible representations \( r \) contained within some reducible representation: we "dot" the character of the reducible representation with the character of each of the irreducible representations as follows

\[
n_r = \frac{1}{N_G} \sum_{\{G\}} \chi(G) \chi^r(G)
\]

where \( N \) is the order of the point group, here eight. In the case of \( \chi^{\nabla \nabla \phi} \{G\} = \{4, 4, 0, 0, 0\} \) we find

\[
\begin{array}{cccccc}
n_{A_1} & n_{A_2} & n_{B_1} & n_{B_2} & n_E \\
1 & 1 & 1 & 1 & 0
\end{array}
\]

and therefore there is one scalar to be found within \( \nabla \times \nabla \times \phi \). A systematic method for determining this scalar is to construct the projection operator onto the scalar subspace

\[
P_{A_1} = \frac{1}{N_G} \sum_{\{G\}} G.
\]

This projection operator, acting on each element of the direct product space, yields a (not generally orthonormal) set of scalars. From these one can choose a linearly independent set of scalars. The process is straightforward, but unenlightening. An alternative, somewhat more clever, way to determine the scalar is to recall that \( \phi \) is a \( B_1 \)-object, and even powers of \( B_1 \)-objects are scalars. Judging from the appearance of \( \phi \), (that is, \( \partial_x U_x - \partial_y U_y \)), one can immediately guess, and quickly check, that \( (\partial_x^2 - \partial_y^2) \) is a \( B_1 \)-object, and that their product is a scalar. Thus, the single scalar which is second order in gradients and first order in the order parameter is \( (\partial_x^2 - \partial_y^2)\phi \).

This intriguing scalar warrants further comment. Reexpressing it,

\[
(\partial_x^2 - \partial_y^2)\phi = \nabla \cdot \left( \begin{array}{c} \partial_x \phi \\ -\partial_y \phi \end{array} \right)
\]

(A9)
we note that it is a total divergence and in the thermodynamic limit it will not contribute to the free energy density. This is easily shown by invoking Green's Theorem which equates the integral of $\nabla \cdot \mathbf{v}$ over an area $\Omega$ with the integral of $\mathbf{v}$ over the area's boundary $C$. Applying this to our present problem, we see

$$\int_{\Omega} \nabla \cdot \left( \begin{array}{c} \partial_x \phi \\ -\partial_y \phi \end{array} \right) \, da = \oint_{C} \left( \begin{array}{c} \partial_x \phi \\ -\partial_y \phi \end{array} \right) \cdot \, d\Gamma$$

where the surface term can only contribute negligibly to the free energy density for any physically meaningful integrand.

An exception to the above conclusion arises when there are defects in the order parameter field. Green's Theorem relies on continuity and continuous differentiability of the relevant vector field: assumptions which break down in the presence of defects. In certain systems, however, defects are fundamental features of the order parameter field, and total divergence terms in the free energy will be important determinants of the ultimate structure of the system. Such a situation arises in cholesteric liquid crystals, giving rise to the blue phases between the cholesteric and isotropic fluids.\textsuperscript{132,133} A total divergence term which is usually discarded from the Oseen-Frank elastic equations for liquid crystals is shown to yield non-zero contributions in the presence of disclination lines. Allowing for disclinations and accounting for their contribution to the free energy makes for a spectacular set of equilibrium phases which are in many ways reminiscent of tweed: they modulate between local regions of high symmetry and low symmetry, and combine low-symmetry regions of various orientations into regular structures. The total divergence scalars we have found, such as the term $(\partial_x^2 - \partial_y^2) \phi$ constructed above and other terms to follow, potentially have the same capacity for generating interesting phases in an elastic medium, just as the previously neglected disclination term has lead to the blue phases.
We have not studied the prospect for such phases, nor have we come across experimental evidence to suggest their existence in solid materials. Still, the excessive population of defects even in “perfect” real crystals suggests that we neglect total divergences only at the risk of passing over subtle and intriguing effects in real materials.

We return to the problem of constructing scalars, now proceeding to the space $\nabla \times \nabla \times \phi \times \phi$, whose character is $\chi^{\nabla\nabla\phi\phi} = \{4, 4, 0, 0, 0\}$. The standard procedure (see eq. (A7)) is used to determine the number of each irreducible representation,

\[
\begin{array}{cccccc}
 n_{A_1} & n_{A_2} & n_{B_1} & n_{B_2} & n_E \\
 1 & 1 & 1 & 1 & 0 \\
\end{array}
\]

and we see that there is one scalar in the space $\nabla \times \nabla \times \phi \times \phi$. Again, one can construct and systematically apply the projection operator to each of the elements of the direct product space, and extract the linearly independent scalars from the results. However, in preparation for terms to be encountered below, where the systematic method is increasingly tedious, we again offer a somewhat more deft derivation. We have noted already that $\phi^2$ is a scalar, and we well know that $\nabla^2 = (\partial_x^2 + \partial_y^2)$ is a scalar. This immediately gives us the scalar $(\partial_x^2 + \partial_y^2)\phi^2$.

In light of the earlier warning to regard permutation of indices with suspicion, the reader may have noticed that there is in fact a multiplicity of scalars which satisfy the above form:

$$(\nabla\phi) \cdot (\nabla\phi), \quad \phi \nabla^2 \phi, \quad \nabla \cdot (\nabla \phi^2), \quad \text{and} \quad \nabla \cdot (\phi \nabla \phi).$$
(A11)

It is necessary to check whether these terms are all linearly independent, and if not, how many of them must be retained. Simple application of the chain rule
tells us that
\[ \frac{1}{2} \nabla^2 \phi^2 = \nabla \cdot (\phi \nabla \phi) = \phi \nabla^2 \phi + (\nabla \phi) \cdot (\nabla \phi), \] (A12)
and therefore there are two equations relating the four invariants, allowing us to retain two of our choosing. We note that the last two terms are total divergences and, as discussed above, will integrate to zero in a defect free system. The scalar \((\nabla \phi) \cdot (\nabla \phi)\) has the convenient appearance of the standard Ginzburg gradient term. This result is satisfying, as the objective has been simply to generate some gradient term (with hopefully positive coefficient for real materials) in order to avoid unrestrained short wavelength deformations in this model.

A.1.3 Scalars Coupling \(\eta\) and \(\phi\): The next step is to investigate allowed ways of coupling a composition field to the order parameter. The composition field, \(\eta\), is simply a value reflecting the local binary alloy composition or concentration of some dopant. It is simply a scalar, its character is of course \(\chi^\eta \{G\} = \{1, 1, 1, 1, 1\}\), and reducing the direct product space of \(\eta\) with any other representation is a rather straightforward exercise: all scalars can be constructed by taking scalars previously found and multiplying by any power of \(\eta\).

The single scalar so constructed which has entered into the bulk of this research is the term \(\eta \phi^2\). It is the simplest coupling between composition and the order parameter that can be written down, and since it couples composition to \(\phi\) in the same way that it couples temperature to \(\phi\), it incorporates into the Landau-Ginzburg model the observed relationship between composition and transition temperature in the real-world materials in a uncontrived way.

There exists another low order scalar which couples composition and the order parameter. The total divergence scalar \((\partial_x^2 - \partial_y^2)\phi\) discussed above leads to
Table A2  Scalars for the two dimensional system.

<table>
<thead>
<tr>
<th>Product Space</th>
<th>Scalar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\prod^n_1 \phi$</td>
<td>$\phi^{2n}$</td>
</tr>
<tr>
<td>$\nabla \times \nabla \times \phi$</td>
<td>$(\partial^2_x - \partial^2_y) \phi$</td>
</tr>
<tr>
<td>$\nabla \times \nabla \times \phi \times \phi$</td>
<td>$(\nabla \phi) \cdot (\nabla \phi)$</td>
</tr>
<tr>
<td></td>
<td>$\nabla \cdot (\nabla \phi^2) \uparrow$</td>
</tr>
<tr>
<td>$\eta \times \prod^n_1 \phi$</td>
<td>$\eta \phi^{2n}$</td>
</tr>
<tr>
<td>$\eta \times \nabla \times \nabla \times \phi$</td>
<td>$\phi(\partial^2_x - \partial^2_y) \eta$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\partial^2_x - \partial^2_y) \phi$</td>
</tr>
<tr>
<td></td>
<td>$\nabla \cdot (\partial^2_x - \partial^2_y) \eta \phi \uparrow$</td>
</tr>
</tbody>
</table>

the coupling term: $\phi(\partial^2_x - \partial^2_y) \eta$ (and other invariants which are equivalent modulo surface terms). Finally, another simple coupling to composition is term $\eta e_1$, which couples to the bulk dilatational strain, rather than the order parameter $\phi$. These terms are further discussed in Chapter 9.

The scalars produced for the two dimensional system are summarized in Table A2. Total divergence terms are denoted by a dagger. Where several different linearly dependent scalars exist, a linearly independent set of the most useful form has been listed.

A.2 Three Dimensions: The Point Group $O_h$

In analogy with the previous treatment for the case of the two dimensional system, this section outlines the derivation of scalars for the three dimensional system, where the order parameter is now $\phi = (\frac{-\varepsilon_{zz} - \varepsilon_{yy} + 2\varepsilon_{zz}}{\sqrt{6}}, \frac{\varepsilon_{zz} - \varepsilon_{yy}}{\sqrt{2}})$ and the scalars must be invariant with respect to the point group $O_h$. Above is
Table A3 The character table for the O point symmetry group.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>8C3</th>
<th>3C2</th>
<th>6C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>F1</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>F2</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Given the character table for the point group O, which is technically incomplete in that it contains only the twenty-four proper symmetries out of the forty-eight symmetries of the full cubic point O_h, (i.e., those symmetries which preserve handedness). However, the full point group is a simple extension of the group shown, O_h = O \times C_i where C_i is the inversion operator. Here, for pedagogical clarity we shall generate scalars of the point group O, and simply note afterward that the resulting scalars are invariant under inversion and therefore scalars of the full point group O_h.

The O_h symmetries are as follows: E is the identity, C_3 is a rotation through angle 2\pi/3 around a body diagonal, C_4^2 is a rotation through angle \pi around a fourfold symmetry axis passing through the centers of opposite faces, C_2 is a rotation through angle \pi around a twofold symmetry axis passing through midpoints of opposite edges, and C_4 is a rotation through angle \pi/2 around a fourfold symmetry axis passing through the centers of opposite faces.

A.2.1 Scalars Constructed from \phi: Repeating the procedure followed in the proceeding section, we give the transformation matrices for a member of each
symmetry class corresponding to the three dimensional vector representation:

\[
E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \quad C_4^2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]

(A13)

The representation for the three component object \((e_{xz}, e_{yy}, e_{zz})\) trivially follows

\[
E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \quad C_4^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]

(A14)

and the representation for the order parameter \(\phi = (\frac{e_{xx} - e_{yy} + 2e_{zz}}{\sqrt{6}}, \frac{e_{xx} - e_{yy}}{\sqrt{2}})\) is straightforwardly derived:

\[
E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad C_3 = \frac{1}{2} \begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}, \quad C_4^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad C_4 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\]

(A15)

Immediately, we note its character \(\chi^\phi = \{2, -1, 2, 0, 0\}\), and conclude that the order parameter is in fact the two component irreducible representation, and transforms as an E-object.

For completeness, we note that the strain space \(\nabla \times U\) decomposes into irreducible representations as follows:

<table>
<thead>
<tr>
<th>Subspace</th>
<th>Character</th>
<th>Irreducible Rep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi_1, \phi_2)</td>
<td>{2, -1, 2, 0, 0}</td>
<td>E</td>
</tr>
<tr>
<td>(e_{xz} + e_{yy} + e_{zz})</td>
<td>{1, 1, 1, 1, 1}</td>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
<tr>
<td>(e_{yz}, e_{zz}, e_{xy})</td>
<td>{3, 0, -1, 1, -1}</td>
<td>F&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>(\omega_{yz}, \omega_{zz}, \omega_{xy})</td>
<td>{3, 0, 1, -1, -1}</td>
<td>F&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
Here, the antisymmetric objects \( \omega_{ij} \equiv (\partial_i U_j - \partial_j U_i) \) measure the rotational component of the strain field. It corresponds to a vector, (i.e. \( F_1 \)-object,) which is the familiar rotation vector describing the direction and magnitude of rotational displacement.

We first consider the space \( \phi \times \phi \), which has a character \( \chi^{\phi \phi} = \{4, 1, 4, 0, 0\} \) and hence has the following decomposition:

\[
\begin{array}{cccccc}
N_{A_1} & N_{A_2} & N_E & N_{F_1} & N_{F_2} \\
1 & 1 & 1 & 0 & 0
\end{array}
\]

Again, we bypass the systematic projection operator approach in favor of a quick argument for the obvious result. Recalling that \( (\phi_1, \phi_2, e_1) \) spans the same space as \( \hat{e} \equiv (e_{xx}, e_{yy}, e_{zz}) \), we find the scalars contained in the space \( \hat{e} \times \hat{e} \) and easily extract those which reside in the subspace \( (\phi_1, \phi_2) \). It is clear that the following two objects are scalars:

\[
(e_{xx} + e_{yy} + e_{zz})^2 \quad \text{and} \quad e_{xx}^2 + e_{yy}^2 + e_{zz}^2 \quad (A16)
\]

To confirm that these are the only scalars, note \( \chi^{\hat{e} \hat{e}} = \{9, 0, 9, 1, 1\} \) (see Eq. (A14)), and therefore contains just two scalars:

\[
\begin{array}{cccccc}
N_{A_1} & N_{A_2} & N_E & N_{F_1} & N_{F_2} \\
2 & 1 & 3 & 0 & 0
\end{array}
\]

Since

\[
\phi_1^2 + \phi_2^2 + e_1^2 = e_{xx}^2 + e_{yy}^2 + e_{zz}^2,
\]

we can immediately conclude that the scalar we seek is

\[
\phi_1^2 + \phi_2^2 = e_{xx}^2 + e_{yy}^2 + e_{zz}^2 - \frac{1}{3} (e_{xx} + e_{yy} + e_{zz})^2. \quad (A17)
\]

For future reference, we look at the other irreducible representations within the \( \phi \times \phi \) space. First, we note that the antisymmetric direct product space has
character $\chi_{anti} = \{1,1,1,-1,-1\}$, i.e. it is an $A_2$-object. (Of course, it is zero for the present case, in which the direct product is being taken between two identical $E$-objects, and the antisymmetric space vanishes.) The remaining two objects in the $\phi \times \phi$ space must be the irreducible representation $E$. The above arguments apply also to the general case of a direct product of two unequal $E$-objects, and we collect the results in the following table:

<table>
<thead>
<tr>
<th>Subspace</th>
<th>Character</th>
<th>Irreducible Rep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_1 \varphi_1 + \phi_2 \varphi_2$</td>
<td>${1,1,1,1}$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$\phi_1 \varphi_2 - \phi_2 \varphi_1$</td>
<td>${1,1,1,-1,-1}$</td>
<td>$A_2$</td>
</tr>
<tr>
<td>$(\phi_1 \varphi_1 - \phi_2 \varphi_2)$</td>
<td>${2,-1,2,0,0}$</td>
<td>$E$</td>
</tr>
<tr>
<td>$- (\phi_2 \varphi_1 + \phi_1 \varphi_2)$</td>
<td>${2,-1,2,0,0}$</td>
<td>$E$</td>
</tr>
</tbody>
</table>


We now proceed to the third order scalar extracted from the space $\phi \times \phi \times \phi$. It is safe to take the character of the symmetric subspace:

$$\chi_{sym}^{\phi\phi\phi}(G) = \frac{1}{6} \left\{ \chi^3(G) + 3\chi(G)\chi(G^2) + 2\chi(G^3) \right\} \tag{A18}$$

and we get $\chi_{sym}^{\phi\phi\phi} = \{4,1,4,0,0\}$. The decomposition is

<table>
<thead>
<tr>
<th>$n_{A_1}$</th>
<th>$n_{A_2}$</th>
<th>$n_E$</th>
<th>$n_{F_1}$</th>
<th>$n_{F_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Again, we can quickly deduce the scalar. We know from the previous argument how to construct a scalar from two $E$-objects, and we see from the above table how to produce an $E$-object from two $E$-objects. Carrying this out, we see the third order scalar is

$$\left( \phi_1 \right) \cdot \left( \phi_1 \phi_1 - \phi_2 \phi_2 \right) \left( \phi_2 \right) \cdot \left( -(\phi_2 \phi_1 + \phi_1 \phi_2) \right) \tag{A19}$$
To find the fourth order scalar, we take the character of the symmetric subspace,
\[
\chi^{\phi\phi\phi\phi}(G) = \frac{1}{24} \left\{ \chi^4(G) + 6 \chi^2(G) \chi(G^2) + 8 \chi(G) \chi(G^3) + 3 \chi^2(G^2) + 6 \chi(G^4) \right\}
\]
and get \(\chi_{\text{sym}}^{\phi\phi\phi\phi} = \{5, -1, 5, 0, 0\}\), with the corresponding decomposition

\[
\begin{array}{ccccc}
n_{A_1} & n_{A_2} & n_E & n_{F_1} & n_{F_2} \\
1 & 0 & 2 & 0 & 0
\end{array}
\]

The single fourth order scalar follows immediately from the second order scalar which we have already found:

\[
(\phi_1^2 + \phi_2^2)^2
\]

**A.2.2 Scalars Constructed from \(\nabla\) and \(\phi\):** As discussed in Chapter 5, these three terms are sufficient to produce a first order transition, so we proceed to the gradient terms. To linear order in gradient and order parameter, there is no scalar: \(\chi^{\nabla\phi} = \{6, 0, -2, 0, 0\}\) has the decomposition

\[
\begin{array}{ccccc}
n_{A_1} & n_{A_2} & n_E & n_{F_1} & n_{F_2} \\
0 & 0 & 0 & 1 & 1
\end{array}
\]

For future reference we will determine the form of the \(F_1\) and \(F_2\) objects which are contained in this space. We recall that the object \(\tilde{\phi} \equiv (\tilde{\phi}_x, \tilde{\phi}_y, \tilde{\phi}_z)\) as defined in Chapter 5 can be expressed in terms of \(\phi = (\phi_1, \phi_2)\) and that it transforms in a straightforward manner. From this we can easily guess the form of the vector contained in this space. It is easily shown that

\[
\begin{pmatrix}
\partial_x \tilde{\phi}_x \\
\partial_y \tilde{\phi}_y \\
\partial_z \tilde{\phi}_z
\end{pmatrix} \equiv \begin{pmatrix}
\partial_x (\phi_1 + \sqrt{3}\phi_2) \\
\partial_y (\phi_1 - \sqrt{3}\phi_2) \\
2\partial_z \phi_1
\end{pmatrix}
\]

(A22)
transforms as a vector, (an $F_1$-object.) The remaining terms in the space $\nabla \times \phi$ are easily seen to compose the $F_2$-object:

$$
\begin{pmatrix}
\partial_x (\tilde{\phi}_y - \tilde{\phi}_z) \\
\partial_y (\tilde{\phi}_z - \tilde{\phi}_x) \\
\partial_z (\tilde{\phi}_x - \tilde{\phi}_y)
\end{pmatrix}
= 
\begin{pmatrix}
\partial_x (\sqrt{3}\phi_1 + \phi_2) \\
\partial_y (\sqrt{3}\phi_1 - \phi_2) \\
2\partial_z \phi_2
\end{pmatrix}
$$

These objects are used below to construct the remaining scalars.

Considering the space $\nabla \nabla \phi$, we get $\chi^{\nabla \nabla \phi} = \{6, 0, -2, 0, 0\}$ has the decomposition

$$
\begin{array}{cccccc}
n_{A_1} & n_{A_2} & n_E & n_{F_1} & n_{F_2} \\
0 & 0 & 0 & 1 & 1
\end{array}
$$

We know how to construct a vector from $\nabla \times \phi$ (see above) so we can immediately conclude that the scalar in $\nabla \times \nabla \times \phi$ is

$$
\nabla \cdot \begin{pmatrix}
\partial_x (\sqrt{3}\phi_1) \\
\partial_y (\sqrt{3}\phi_1) \\
2\partial_z \phi_2
\end{pmatrix}
$$

Just as in the case of the $\nabla \times \nabla \times \phi$ scalar for the two dimensional case, the scalar constructed here is a total divergence, and we can apply Gauss's Theorem, (the three dimensional analog of Green's Theorem), to equate the volume integral of this total divergence with the surface integral of its field. In precise analogy with the two dimensional case, this allows us to conclude that this term would contribute negligibly to a total free energy density, providing that the order parameter field does not have a finite density of defects. See the previous discussion of the rediscovered total divergence term and blue phases in cholesteric liquid crystals.

We now proceed to the space $\nabla \times \nabla \times \phi \times \phi$. The character, $\chi^{\nabla \nabla \phi \phi} = \{36, 0, 4, 0, 0\}$, and the decomposition
suggest the existence of two scalars, which are immediately constructed from the F₁ and F₂ objects found above simply by taking the square (inner product) of each term:

\[
\begin{align*}
\left( \frac{\partial_x (- \phi_1 + \sqrt{3} \phi_2)}{2 \partial_x \phi_1} \right)^2 & \quad \text{and} \quad \left( \frac{\partial_y (- \phi_1 - \sqrt{3} \phi_2)}{2 \partial_x \phi_1} \right)^2 \\
\left( \frac{\partial_x (- \sqrt{3} \phi_1 + \phi_2)}{2 \partial_x \phi_1} \right)^2 & \quad \text{and} \quad \left( \frac{\partial_y (\sqrt{3} \phi_1 - \phi_2)}{2 \partial_x \phi_1} \right)^2
\end{align*}
\]

As in the two dimensional case above, there are four different terms which satisfy this form, and there are two relations (provided by applications of the chain rule) relating the terms, leaving us free to choose two independent terms.

**A.2.3 Scalars Coupling \( \eta \) and \( \phi \):** Finally, we consider the coupling of the composition field \( \eta \) to the order parameter. Recall, \( \eta \) is a scalar and will not affect the group representation of any object which it multiplies, so we can produce scalars coupling composition and the order parameter from any scalars found thus far. The simplest term so devised is \( \eta (\phi_1^2 + \phi_2^2) \). Other terms analogous to the two dimensional case exist. In particular the term arising form the total divergence term in the space \( \nabla \times \nabla \times \phi \),

\[
\begin{align*}
\left( \frac{- \phi_1 + \sqrt{3} \phi_2}{2 \phi_1} \right) \cdot \left( \begin{array}{c} \partial_x^2 \\ \partial_y^2 \\ \partial_z^2 \end{array} \right) \eta \\
\left( \frac{- \phi_1 - \sqrt{3} \phi_2}{2 \phi_1} \right)
\end{align*}
\]

and the linear coupling to bulk dilatation \( \eta e_1 \). The physics underlying these terms is precisely analogous to the two dimensional case, and much of the discussion in Chapter 9 applies.

We summarize the results in Tables A4 and A5, in which the scalars which have been produced are expressed both in terms of our order parameter \( \phi = \)
Table A5 Scalars for the three dimensional system.

<table>
<thead>
<tr>
<th>Product Space</th>
<th>Scalar</th>
<th>Scalar</th>
<th>Scalar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>$(\phi_1, \phi_2)$</td>
<td>$\phi$</td>
<td>$(\phi_1, \phi_2)$</td>
</tr>
<tr>
<td>$\phi \times \phi$</td>
<td>$\phi_1 \phi_2 - \phi_2 \phi_1$</td>
<td>$\phi_1 \phi_2 - \phi_2 \phi_1$</td>
<td>$\phi_1 \phi_2 - \phi_2 \phi_1$</td>
</tr>
<tr>
<td>$\phi \times \phi \times \phi$</td>
<td>$\phi_1 \phi_2 \phi_3 - \phi_2 \phi_3 \phi_1$</td>
<td>$\phi_1 \phi_2 \phi_3 - \phi_2 \phi_3 \phi_1$</td>
<td>$\phi_1 \phi_2 \phi_3 - \phi_2 \phi_3 \phi_1$</td>
</tr>
</tbody>
</table>

$(\phi_1, \phi_2)$ and the tetragonal strains $\phi = (\phi_x, \phi_y, \phi_z)$. Total divergence terms are denoted by a dagger.
### Table A5  Scalars for the three dimensional system, continued.

<table>
<thead>
<tr>
<th>Product Space</th>
<th>Scalar</th>
<th>Scalar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta \times \phi \times \phi$</td>
<td>$\eta (\phi_1^2 + \phi_2^2)$</td>
<td>$\eta (3 \sum \phi_i^2 - (\sum \phi_i)^2)$</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\eta \times \phi \times \phi &= \left( -\phi_1 + \sqrt{3}\phi_2 \right) \cdot \left( \frac{\partial \phi_1}{\partial x} \right) \eta \quad \phi \cdot \left( \frac{\partial \phi_1}{\partial y} \right) \eta \\
\eta \left( \frac{\partial \phi_2}{\partial y} \right) \cdot \left( -\phi_1 - \sqrt{3}\phi_2 \right) &= \eta \left( \frac{\partial \phi_2}{\partial y} \right) \cdot \phi \\
\nabla \cdot \left( \frac{\partial x}{\partial y} \eta (\phi_1 + \sqrt{3}\phi_2) \right) &= \nabla \cdot \left( \frac{\partial x}{\partial y} \eta (\phi_1 - \sqrt{3}\phi_2) \right) \nabla \cdot \left( \frac{\partial z}{\partial y} \eta \phi_1 \right)
\end{align*}
\]
Appendix B

Some Energy Balance Arguments for Tweed Length Scales

In this Appendix, we offer, in the spirit of Imry and Wortis\textsuperscript{84}, some brief energy scale arguments for estimating the length scale of tweed.

A rough estimate of $L$ and $\xi$ can be obtained by balancing the dominant energies in the tweed problem. The first of the important energy scales is the energy gained by the coupling between the $\phi$ strain and the the composition field $\eta(x, y)$. There is one degree of freedom in each correlated region of area $\sim L\xi$, and in this area, the statistical variation in the composition inhomogeneity will scale as the inverse square root of the area:

$$\Delta \eta = a \sqrt{\frac{\eta_0 (1 - \eta_0)}{L\xi}}$$  \hspace{1cm} (B1)

where $a$ is the lattice constant and the term $\eta_0 (1 - \eta_0)$ reflects fluctuations about some mean $\eta_0$, and is typically of order unity. Since the composition variations couple through the free energy term $A_\eta \Delta \eta \phi^2$, the energy density gained from the impurity coupling is

$$E_{\text{disorder}} \sim -A_\eta \phi_0^2 a / \sqrt{L\xi}$$  \hspace{1cm} (B2)

where $\phi_0 \sim$ martensitic strain.

The second important energy scale results from the bulk dilation and diagonal strain needed to accommodate the elastic compatibility constraints, which we can estimate in the following way. As discussed in Chapter 7, we can write the general displacement fields in the form

$$U(x, y) = \left( \begin{array}{c} 1 \\ -1 \end{array} \right) U_+ \left( \begin{array}{c} x + y \\ \frac{x - y}{L} \end{array} \right) + \left( \begin{array}{c} 1 \\ 1 \end{array} \right) U_- \left( \begin{array}{c} x + y \\ \frac{x - y}{L} \end{array} \right)$$  \hspace{1cm} (B3)
where for a tweedy deformation the anisotropy in the displacement field can be absorbed into the correlation lengths $L$ and $\xi$, and the functional forms $U_+$ and $U_-$ are defined to be isotropic and therefore have comparable gradients in their two variables, (which we'll generically denote $U'$). Immediately, we can compare magnitudes of the different components of the strain field:

$$e_1 = U_{xx} + U_{yy} \sim U' / L$$

(B4a)

$$e_2 = U_{xy} + U_{yx} \sim U' / L$$

(B4b)

$$\phi = U_{xx} - U_{yy} \sim U' / \xi$$

(B4c)

and therefore $e_1$ and $e_2$ are $O(\phi \xi)$. We see then that the secondary strains grudgingly generated as the material responds to the compositional disorder has a energy

$$E_{\text{grudge}} = A_1 e_1^2 + A_2 e_2^2 \sim (A_1 + A_2) \phi_0^2 (\frac{\xi}{L})^2$$

(B5)

Balancing these two energy scales gives us an estimate for the length scale of the tweed domain size

$$L \sim \xi^{5/3} / (\epsilon \alpha)^{2/3}$$

(B6)

Here $\epsilon = A_\eta / (A_1 + A_2)$ is a small parameter reflecting the relative strength of the coupling to composition and the elastic energies associated with bulk and diagonal strains. The parameters from FePd used in the simulation give $\epsilon \sim 1/20$, and therefore Eq.(B6) implies $L \gg \xi$ as we would expect.

The final important energy scale is the gradient energy which resists order parameter variations:

$$E_{\text{gradient}} = \kappa (\frac{\phi_0}{\xi})^2$$

(B7)

This energy is balanced against other energies, determining $\xi$:

$$\xi \sim \frac{(\kappa / (A_1 + A_2))^{3/2}}{(\epsilon \alpha)^2}.$$
The resulting length scales are then $\xi \sim 5$ and $L \sim 100$, in surprisingly good agreement with our simulation, considering the fact that equations (B6) and (B8) are highly sensitive to small changes in parameters.

For comparison to the calculations in Chapter 7, note that equations (B6) and (B8) suggest the following dependences on the strength of disorder:

$$L \sim A^{-4}_\eta \quad \text{and} \quad \xi \sim A^{-2}_\eta.$$  

(B9)
Appendix C

Simulation Images (Black/White Versions)
Figure 6.1 Configurations Generated by Numerical Simulation (See text for explanation.)
Figure 6.2 Configurations Generated by Numerical Simulation (See text for explanation.)
Figure 6.3 Configurations Generated by Numerical Simulation (See text for explanation.)
Figure 7.6  The displacement field $U(x, y)$ projected onto the (11) direction, yielding $U_-(x - y)$. 
Figure 9.2  The configuration resulting from a linear coupling to bulk shows no identifiably tweedy modulation.
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