LINE DEFECTS AND GAUGE INVARIANCE IN GLASSES

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ABSTRACT

In this thesis we discuss two distinct classes of defects in glasses, which affect the low temperature thermodynamics and high temperature relaxation properties. The first class, the intrinsic defects, arise from the constraints of the underlying network and are, therefore, present even in perfect glasses. The second class, the topological excitations, take the form of Z_2 line defects. The temperature dependence of the equilibrium density of topological defects is such that they lead to a universal explanation of the Vogel Fulcher Law for the viscosity of supercooled liquids.

Further insight into the nature of the defects is gained by studying a field theory in which the overall homogeneity of glass is formulated as a local invariance of the free energy. Here the topological line defects are analogous to vortices of type II superconductors. Intrinsic defects, in the form of lines of curvature, act as sources of the field and introduce energy density fluctuations. Each such defect is associated with two equal energy solutions of the Euler Lagrange equations, related

by a nontrivial gauge transformation. Such two level systems could be responsible for the anomalous low temperature properties of glasses.

An alternative field theory is discussed in which the continuum spin glass model is derived from the Edwards Anderson Hamiltonian, with intrinsic defects (frustration lines) included as lines of finite curvature. The topological excitations are vortices of the spin field. It was necessary to approach the continuum model for an atomic glass from a macroscopic point of view. The model is that of an isotropic elastic continuum with torsion and curvature included to describe the ring closure constraints of the underlying network. Here the topological defects are 2π disclinations. In both spin glass and atomic glass the reversal of the orientation of an intrinsic defect line constitutes a specific model for the two level system.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

At first sight the task of identifying defects in glasses might appear rather futile since glasses, unlike crystals, do not have any long range order or, indeed, any unique ideal configuration. Many of the properties of glasses are, however, strongly suggestive of the presence of defects, although the precise nature of these objects is not apparent. Metallic glass exhibits a mode of plastic deformation which closely resembles that mediated by dislocations in crystals. Magnetostriction experiments (Grimm and Kronmüller 1980) have revealed dislocation like sources of strain in ferromagnetic glasses. Indeed, any rapidly quenched glass relaxes to a lower energy configuration on annealing below the glass transition temperature and such a process could be due to the annihilation of defects. An almost universal feature of the glassy state is the anomalous low temperature thermodynamic and acoustic behaviour. It is possible that defects exclusive to glasses are responsible for such behaviour.

In the first chapter of this thesis we summarize some of the universal properties of glasses and review the various methods which have been used to identify defects in these materials. In chapter 2 we discuss one such method which predicts the existence of topologically stable line defects in amorphous materials, and show how they can be used to explain the observed relaxation behaviour of supercooled liquids. In chapter 3 we develop a phenomenological gauge invariant field theory of glasses in which the topological defects resemble vortices in superconductors. They are present in the glass, in thermal equilibrium, at finite temperature and diffuse freely in the medium. Other defects, in the form of quenched lines of finite curvature, are present at all temperatures and these have the effect of introducing a number (two per defect) of distinct ground state configurations, related to each other by non trivial gauge transformations. A continuum version of the Edwards Anderson Model of a spin glass is derived in chapter 4, with frustration included as lines of finite curvature. These introduce low energy excitations which are equivalent to the reversal of the orientation of a frustration line. Here the topological defects are vortices of the spin field. In chapter 5 we express the Keating Model of covalent materials in a representation which resembles the Edwards Anderson model of spin glass and include the ring closure constraints as torsion and curvature. The random bond directions inhibit the passage to the continuum limit in this model. In chapter 6 a glass is considered, from a macroscopic point of view, as an isotropic elastic continuum with torsion and curvature. Again the presence of these defects introduces low energy excitations which correspond to reversing the orientation of a line. In this case the topological defects are disclinations with the distortion field screened by dislocations. We conclude, in chapter 7, with a general discussion and a comparison of the three continuum models. Although the models vary significantly in detail, the general features are very similar. In particular, each has two distinct types of defect, one type affecting the low temperature properties and the other, the topological defects, dominating the relaxation processes in supercooled liquids.

The general trend of this thesis goes from a phenomenological (chapter 2 and 3) to a more microscopic description of glasses (chapter 4 and 5), and finally (chapter 6) back to a macroscopic description where the defects introduced earlier, and specific to glasses, appear naturally in the framework of continuum elasticity theory.

1.2 Review of Some Significant Properties of Glasses

1.2.1 The Glass Transition

Unlike the transition from the liquid to the crystalline state, the glass transition is not a true thermodynamic phase transition. It is, in fact, a kinetic transition in that it corresponds to the situation where the timescale required for structural changes to occur becomes longer than the experimental timescale. For a given cooling rate the glass transition temperature (Tg) is the temperature at which the structural relaxation time of the supercooled liquid becomes too long for the liquid to remain in (internal) equilibrium, and it corresponds to a viscosity of the order of 10^{13} poises. Even above Tg a supercooled liquid is not in the true equilibrium state (the crystal always has lower energy) but it is in a metastable or internal equilibrium configuration.

Thus the glass transition temperature is not unique for a given liquid, but it is a function of the cooling rate. The range of variation is, however, very small because the structural relaxation time has a very strong temperature dependence in this region. The glass transition is accompanied by a very rapid, but continuous, change in the slope of the temperature dependence of thermodynamic variables such as the volume, entropy and enthalpy (Figure 1.1). The volume of a supercooled liquid decreases more rapidly with temperature than the volume of the corresponding crystal, but the rate of decrease in the glass and crystal are approximately equal. Kauzmann (1948) noted that both the volume and the entropy of a supercooled liquid fall below the volume and entropy of the corresponding crystal at a finite temperature (To), although this situation (which has become known as the "Kauzmann Paradox") cannot, in fact, be reached because the glass transition always intervenes. Gibbs and DiMarzio (1958) noted that the Kauzmann Paradox is resolved if a true (but inaccessible) second order phase transition involving a discontinuity in the temperature derivative of the entropy, occurs at To. The mechanism which they have suggested for the transition, based on counting polymer like configurations, has been criticized by Gujrati and Goldstein (1980, 1981).

A second striking feature of supercooled liquids is the temperature dependence of the transport properties, which follow a universal law known as the Vogel Fulcher Law (Vogel 1921, Fulcher 1925):

$$\eta^{-1} = \eta_0^{-1} \exp - \frac{A}{T-To} \qquad 1.1$$

Here η^{-1} represents the inverse viscosity but the self diffusion rate, nuclear spin relaxation rate and all other relaxation rates follow the same law with the same value for the constants (A,To) in a given material. Here To is the same temperature where Kauzmann's paradox occurs. The law has been observed in materials as different as polymers (Kovacs 1973) organic liquids (Barlow et al 1967), ionic liquids (Angell et al 1967) and metallic liquids (Chen and Goldstein 1972). Recently

Toulence (1980) measured the frequency dependence of the susceptibility cusp of a spin glass and found evidence that the spin relaxation time follows a similar law.

The oldest explanation of this behaviour is the free volume theory of Cohen and Turnbull (1959, 1961). The theory has recently been extended (Cohen and Grest 1979) in such a way that it can be used to explain the thermodynamics of the transition. The argument is based on the assumption that flow, or relaxation, can only occur at a given site when a large enough hole (volume Vo) opens up next to the site. Thus if the fractional excess volume per site (with the close packed state taken as reference) is $V_F = V - Vo$ then the probability of finding a hole of size Vo is proportional to $\exp(-Vo/V_F)$ and $\eta^{-1} \alpha \exp - \frac{Vo}{V-Vo}$ 1.2

The assumption that (V-Vo) is proportional to T-To leads to the observed behaviour. There has, however, been a number of objections to this explanation and Anderson (1980) mentions a few. In particular there seems to be no physical justification for the assumption that the excess voume falls linearly to zero at a finite temperature (To). In fact fitting the experimental data to equation 1.2 (the Doolittle law, Doolittle 1951) has not been as successful as equation 1.1. In addition it is difficult to justify the free volume approach for anything other than a hard sphere model of a liquid and this does not seem appropriate for many of the complicated systems in which this behaviour is observed.

A somewhat similar line of approach, involving configurational entropy instead of volume, was taken by Adams and Gibbs (1965). Here a small region of the liquid cannot undergo a change in configuration unless the entropy exceeds a critical value (So) therefore as before,

$$\eta^{-1} \propto \exp - \frac{So}{Sc} \qquad 1.3$$

where Sc is the total configurational entropy. However, in the presence of a second order phase transition at To (Gibbs, DiMarzio 1958) we might expect $Sc \propto (T-To)$ and the Fulcher law is again recovered. It is this expression for Sc which has been criticized by Gujrati and Goldstein (1981).

There has been a number of more recent attempts to derive the Vogel-Fulcher law for the viscosity of supercooled liquids. J.C. Phillips (1981) introduced a model in which the temperature dependence of the size of molecular clusters is responsible for the observed behaviour, but again it is difficult to envisage how such a specific model could explain its occurrence in a wide variety of materials. Cyrot (1981) considered energy fluctuations in supercooled liquid to play a dominant role. Here it is the life time of an infinite amorphous cluster which follows a Vogel Fulcher law. Shtrikman and Wohlfarth (1981) have explained the observation of the Vogel Fulcher law in spin glass in terms of the interaction between magnetic clusters.

In this thesis (chapter 2) we follow a suggestion by Anderson (1980) that the presence of topological defects may be responsible for the universal behaviour of the relaxation time in supercooled liquids, and show that the density of line defects follows equation 1.1 and yields the Vogel Fulcher law for the relaxation time of supercooled liquids.

1.2.2 Low Temperature Properties of Glasses

On a microscopic level a glass looks very different from a crystal however, macroscopically, both systems can be considered to be elastic continua. In other words, when we observe properties which do not depend on the details of the atomic structure we expect a glass to behave in a similar way to a crystal. One such property is the excitation spectrum of long wavelength phonons because the microscopic disorder should be irrelevant when the wavelength is much longer than the interatomic distance. The low temperature specific heat of crystals is dominated by such long wavelength phonons and it tends to zero as the cube of the temperature. Similar behaviour would be expected in a glass if the dominant low energy excitations were phonons, however Zeller and Pohl (1971) measured the low temperature specific heat of vitreous silica, germania and selenium and found a linear temperature variation which dominates the phonon contribution below 1°K. In addition the thermal conductivity was found to vary as the square of the temperature, rather than the cube as in crystals. Similar effects have since been found in polymers (Stephens 1973) and metallic glasses (Graebner et al 1977) and in all other inorganic glasses which have been measured except, it seems, amorphous arsenic. A linear term in the specific heat of dilute magnetic alloys (now known as spin glass) was discovered earlier by Zimmerman and Hoare (1958,1960).

Such behaviour implies that, in addition to long wavelength phonons, glasses have other low energy excitations which affect the thermodynamic properties. Anderson, Halperin and Varma (1972) and W.A. Phillips (1972) independently discussed a model which successfully explained the low temperature anomalies and made predictions which have since been verified (Black 1981). The potential energy surface of a glass in configuration space is very complicated with a number of roughly equivalent "ground states". Most of these are inaccessible to a glass in a particular configuration, however a small fraction of the local minima may be accessible in experimental timescales and these will, therefore, contribute to the specific heat. The magnitude of the linear term of the specific heat (Stephens 1973, 1976) suggests that the probability of finding one such nearby minimum is extremely small, thus it is reasonable to neglect the possibility of a third accessible minimum. Anderson et al and Phillips introduced the concept of the "two level system" which considers part of the potential energy surface containing two minima, separated by a distance d and a barrier of height V (Figure 2.2). At low temperatures, transitions between the two configurations can occur via quantum mechanical tunelling. If Ψ_L and Ψ_R are the wavefunctions corresponding to the left and right well respectively then the Hamiltonian, in terms of these basis states, is

$$H = \tfrac{1}{2} \begin{pmatrix} \Delta & \Delta_o \\ \Delta_o & -\Delta \end{pmatrix} + \begin{pmatrix} \delta & o \\ o & -\delta \end{pmatrix} e \qquad 1.4$$

$$\text{with } \Delta_o = \bar{h}\omega_o \cdot \exp(-\lambda) \qquad 1.5$$

$$\text{and } \lambda = d\bar{h}^{-1} \sqrt{2mV} \qquad 1.6$$

M is the effective mass of the rearranging atoms, e is the strain field and $2\delta = \frac{d\Delta}{de}$. The second term originates in the dependence of the shape of the potential energy surface on the local strain field. In terms of the spin operators ($S\alpha = \tfrac{1}{2}\sigma\alpha$ and $\sigma\alpha$ ($\alpha = 1, 2, 3$) are the Pauli Matrices).

$$H = \Delta S_z - \Delta_o S_x + 2\delta e S_z \qquad 1.7$$

Diagonalizing the first term of equation 1.4 (rewriting it in terms of the basis states $\Psi_\pm = \Psi_R \mathrm{Cos}\,\frac{\Delta o}{2\Delta} \pm \Psi_L \mathrm{Sin}\,\frac{\Delta o}{2\Delta}$)

the Hamiltonian becomes

$$H = E S_z + (M S_x + D S_z)\, e \qquad 1.8$$

with $E^2 = \Delta^2 + \Delta o^2$

$$M = \frac{2\Delta o}{E}\,\delta$$

$$D = \frac{2\Delta}{E}\,\delta$$

The unperturbed ($e = o$) states now have an energy splitting E which is necessarily greater than (or equal to for infinite barriers) the original splitting (Δ). The presence of the off diagonal coupling ($Me\,S_x$) implies that perturbations of the strain field can lead to transitions between the two diagonal states (Ψ_+, Ψ_-).

The contribution of tunnelling states of this kind to the specific heat depends on the distribution of the parameters Δ and Δo. The usual assumption (Black 1978) is that the distribution function is independent of Δ and depends on Δo only through the uniform distribution of barrier heights (V).

i.e $P(\Delta,\lambda) = P(0,\lambda) = \bar{P}$ 1.9

therefore defining $r = \frac{\Delta o^2}{E^2}$, $P(E,r) = \frac{1}{2} r^{-1}(1-r)^{-\frac{1}{2}}\ \bar{P}$ 1.10

The specific heat (Cv) is related to the distribution of eigen states of (1.8) through the expression (Phillips 1972)

$$C_V = k_B \int_0^\infty \int_{ro}^1 dr\, P(E,r) \left(\frac{\beta E}{2}\right)^2 \mathrm{Sech}^2\left(\frac{\beta E}{2}\right) \qquad 1.11$$

$$= \frac{\Pi^2}{6} k_B^2 \; T \,\overline{P} \left[\int_{ro}^1 \frac{dr}{r} \; (1-r)^{-\frac{1}{2}} \right] \qquad 1.12$$

and is indeed linear in the temperature. Here ro is a function of the maximum barrier height consistent with observations in experimental timescales. The magnitude of the linear term in the specific heat implies a density of states of around 10^{19} - 10^{20} eV cm^{-3} and this is consistent with a concentration of two level systems of between 1 and 10 per million atoms (Black 1981).

The strain dependent off diagonal term in equation 1.8 represents the interaction of the two level system with phonons. A phonon of frequency ($\bar{h}^{-1}$ E) can be resonantly absorbed by a two level system with energy splitting E, or it can stimulate the emission from an excited two level system of the same energy. Such processes lead to a phonon mean free path (ℓ) given by (Anderson Halperin and Varma 1972)

$$\ell^{-1} = \frac{\Pi\omega}{\rho V^3} \; \overline{P} \; \delta^2 \tanh \frac{\bar{h}\,\omega}{2k_B T} \qquad 1.9$$

Here ρ is the mass density and V is the sound velocity. The dominant frequency of the thermal phonons is $h\omega = k_B T$ therefore the mean free path (ℓ) of thermal phonons is proportional to the inverse of the temperature and the thermal conductivity, ($K = \frac{1}{3} C_v v \cdot \ell$, with Cv representing the phonon specific heat) is proportional to the square of the temperature, as observed by Zeller and Pohl (1971) and Stephens (1973).

One of the most successful features of the tunnelling model is its ability to explain the saturation of ultrasonic attenuation at high power levels (Hunklinger et al 1972, Golding et al 1973). At low power levels the mean free path of the phonons is dominated by resonant absorption (equation 1.9) but as the power increases the population of the two states equalize and the absorption and emission processes completely cancel, with no net absorption. Hole burning and spin echo experiments have also been carried out successfully in insulating glasses (Hunklinger and Arnold 1976, Golding and Graebner 1976) and these lead to accurate estimates of the relaxation times of the two level system.

The search for similar effects in metallic glass was hindered by the presence of conduction electrons which contribute a large linear term to the specific heat. However this contribution is negligible in experiments carried out below the superconducting transition temperature therefore the linear term in the specific heat observed for Zr Pd in this regime (Graebner et al 1977) is indeed due to the two level system. A T^2 term in the thermal conductivity was observed in the same system. The current state of the observation of two level systems in metallic glass is reviewed by Black (1981).

There have been a number of attempts to identify the microscopic origin of the two level system in glasses. Several possibilities for oxide glasses are presented by Jäckle et al (1976). J.C. Phillips (1980) suggests they may be due to hydrogen atoms tunnelling between two equivalent positions in surface defects of over constrained glasses. W.A. Phillips (1981) discusses a specific model in which an OH^- ion rotates about a SiO bond of amorphous Silica. Villain (1977) showed that the spins on a frustration line in the x-y model of a spin glass have two equivalent ground state configurations (chiralities). As yet, however, no universal explanation has been offered for the effects in such a wide variety of materials. In chapter 3 of this thesis we present a model in which the two level system is a natural consequence of the coexistence of gauge invariance and defects. An alternative explanation is discussed in chapters 4 and 6 where the tunnelling excitations correspond to the reversal of the orientation of defect lines.

1.2.3 Plastic Flow in Metallic Glasses

Metallic glasses exhibit an exciting combination of physical properties for potential technological applications, such as a very high fracture strength, fracture toughness and stiffness. Under high stresses they show some degree of plastic deformation, with two distinct deformation modes:-

(i) Homogeneous deformation at high temperatures and low strain rates.

(ii) Inhomogeneous deformation, concentrated in very narrow shear bands along the direction of maximum shear stress, at low temperatures and high strain rates (Masumoto and Maddin 1971).

Inhomogeneous deformation is mediated by hetrogeneous nucleation of slip, followed by localized spreading. It is a common mode of deformation in crystals where it is nucleated by a dislocation and confined to the slip plane of the dislocation. The appearance of localized slip bands in glasses lead to the suggestion (Gilman 1972) that dislocations (with fluctuating Burger's vector) also exist in amorphous materials. The idea that dislocations can be defined in a medium without order has not been generally accepted therefore several alternative explanations have been discussed. Leamy et al (1972) suggested that plastic flow occurs via the motion of localized strain concentrations. Polk and Turnbull (1972) explained slip localization in terms of strain softening due to structural disordering of the slipped area. Spaepen and Turnbull (1974) assumed that hetrogeneous slip nucleation occurs at a surface defect and the viscosity decrease due to dilation ahead of the crack leads to localized spreading. Li (1976) demonstrated how density fluctuations can cause hetrogeneous nucleation of slip.

In chapter 6 of this thesis we discuss how dislocation like sources of stress and strain are present in glasses at all temperatures. The "dislocations" must obey conservation laws and as such they cause hetrogeneous nucleation and localized spreading of slip. They are the sources of strain and density fluctuations discussed by Leamy (1972) and Li (1976).

1.3 The Identification of Defects in Glasses

In general, the concept of a defect implies the existence of a perfect, defect free state as a reference, with defects being defined as deviations from the reference state. In a crystal, or other ordered medium, the structure of the reference state is known and the identification of defects is almost trivial. In a glass there is no unique reference configuration therefore the above definition of a defect is not very useful, however some glasses are more "perfect" than others because annealing a rapidly quenched glass just below the glass transition temperature causes relaxation towards a lower energy configuration. The perfect or ideal glass is one which has been cooled infinitely slowly from the melt but, of course, this situation can never be achieved in practice.

Although there is no long range order glasses have, in general, a strong degree of short range order which acts as a local reference configuration. For example, each atom of a covalent glass has a similar environment (co-ordination number) to the atoms of the corresponding crystal and deviations from this ideal environment (in the form of dangling bonds) are easily identified as defects. In a metal-metalloid glass (such as PdSi) the ideal surroundings of a metalloid ion is a trigonal prism of metal ions (Gaskell 1979) and deviations from this configuration could be corresponding defect in metal-metalloid glasses.

An alternative definition of a defect which is applicable to glass is that of a source (line or point) of distortion in the medium. A transparent example of such a defect is a frustration line of a spin glass. A simple model of a spin glass is one where the spins reside on a lattice with random ferromagnetic and antiferromagnetic interactions. On any plaquette (elementary face of the lattice) with an odd number of negative bonds, it is impossible to minimize the energy of the spins across all bonds simultaneously (Toulouse 1977) and in three dimensions such frustrated plaquettes are threaded through by lines (frustration lines) which cannot end within the medium. In an Ising model the unsatisfied bonds lie on a plane bounded by the frustration loop therefore the energy is proportional to the area of the loop, but in an x-y model the distortion is shared between all the bonds and the spins relax to a vortex like configuration with an energy of the form L ln L (L is the length of the loop) (Fradkin et al 1978). Thus frustration lines act as sources of distortion to continuous spins in a spin glass model.

Rivier (1979) noted that, like the lines threading frustrated plaquettes, the lines threading rings with an odd number of bonds, in a continuous random network model of a covalent glass, cannot end within the medium. They must form closed loops or end on the surface. Such odd rings (3-fold excepted) are incompatible with any combination of rotational and translational symmetry and are not, therefore, found in crystals, except at the cores of disclination lines. They can thus be considered to be analogous to frustration lines of spin glass. Similar lines can also be identified in a dense random packing model by considering the (dual) network formed by the edges and vertices of the Voronoi polyhedra of the spheres.

On a somewhat different line of approach Kleman and Sadoc (1979) suggested that glasses could be visualized as ordered lattices in spaces of finite curvature, projected in ordinary Euclidean space. The idea arises from the fact that the fundamental unit of the dense random packing model (the configuration which maximizes the local density) is the regular tetrahedron and this does not fill a 3 dimensional Euclidean space, but it does fill a 3 dimensional sphere (a space with constant positive curvature). Mapping a regular structure from the sphere on to Euclidean space not only introduces distortions, but also cut surfaces (wall defects). In a similar way the mapping of a regular structure from a space with constant negative curvature introduces singular lines (disclinations).

The physical parameters of a glass (density, stress, entropy) fluctuate throughout the medium (for direct evidence see Grimm and Kronmüller (1980)) and the extremes of the distribution of the fluctuations can, in some respects, be considered to be defects. An extensive study of the statistical fluctuations in the stress (dilational and shear) field of a computer model of amorphous iron has been carried out by Srolovitz et al (1981) who found that the width of the distribution decreased during relaxation. This can be interpreted to mean that the defects (extremes of the distribution) annihilate each other during this process. Free Volume also falls into this category because it is really the extreme of a continuous distribution of hole size.

Toulouse and Kleman (1976) introduced a scheme in which the topologically stable defects of ordered media can be classified by the behaviour of a field on a surface surrounding the defect (Homotopy theory). It has been suggested (Toulouse 1979, Rivier 1979) that this procedure can also be applied to amorphous media, with the result that the only topologically stable defects in glasses are line defects which are their own antidefects. Homotopy theory, and its application to glasses, are discussed in more detail in chapter 2 of this thesis.

The defects discussed in this section fall naturally into two classes, those which can be eliminated by relaxation (and would not, therefore, be present in a perfect glass) and those which form an intrinsic part of the structure of the glass (at T = 0) and cannot be completely removed by relaxation. Frustration lines in a spin glass are a good example of the latter (intrinsic) defects because their number cannot be reduced by relaxation or cooling at a slower rate through the glass transition temperature. Also in this category are the lines threading odd rings of a continuous random network because, unless a conscious effect is made to avoid them (Connell, Temkin 1974) the average density of odd rings is independent of the model (Weaire 1979). Similarly, the line and surface defects discussed by Sadoc and Kleman are a necessary consequence of the mapping from a curved space to a Euclidean space and cannot, therefore, be eliminated by relaxation.

On the other hand one would not expect to find dangling bonds in a perfect glass and the free volume should also disappear at a finite temperature. Statistical fluctuations cannot be completely eliminated by relaxation but the width of the distribution is decreased. Topological defects are excitations from the "ground state" and would not be present in a fully relaxed glass. We shall see (chapter 2) that they are only present in thermal equilibrium above a finite temperature.

Thus we see that there are a number of alternative approaches to the problem of identifying defects in glasses, but it is important to distinguish between intrinsic defects (which have no crystalline counterpart) and excitations from the "perfect" glassy state. The latter are more in keeping with the usual concept of a defect. We feel that both classes of defect have important consequences in the properties of glasses, with intrinsic defects (in the form of sources of distortion) being responsible for the unusual low temperature properties and topologically stable defects (2Π disclinations) dominating the relaxation at high temperatures. Such features are common to all models of glass discussed in this thesis.

The random orientation of the local environment of the atoms of a glass (or conversely, the macroscopic homogeneity) is expressed mathematically as a local invariance (gauge symmetry) of the free energy. Like defects, gauge invariance is a feature of all models of a glass discussed in this thesis and it has important consequences in the low temperature behaviour of the phenomenological model (chapter 3).

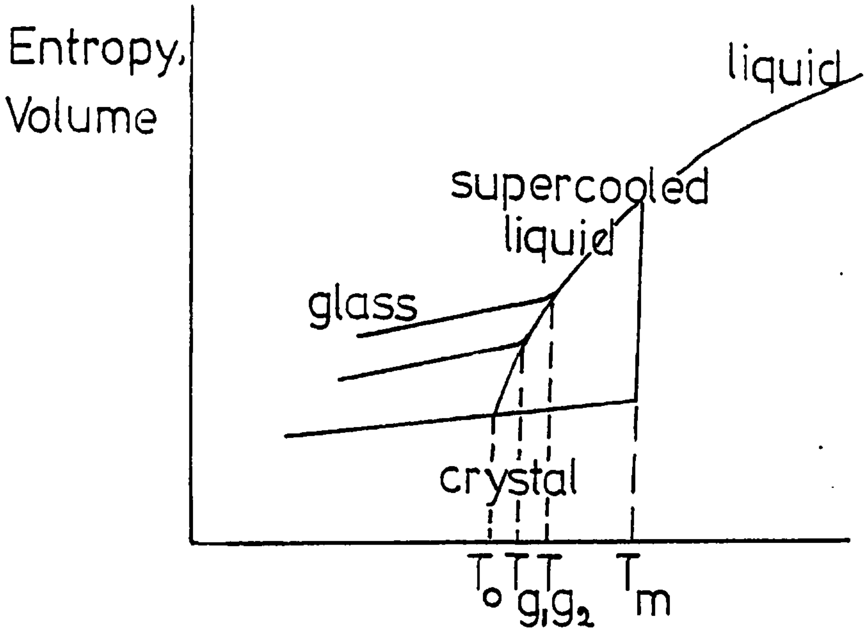


Figure 1.1

Tm is the Melting temperature

Tg_1, Tg_2, glass transition temperature for two different cooling rates, (R_1, R_2). Here $R_2 > R_1$.

To is the temperature at which the entropy of a supercooled liquid becomes equal to that of a crystal.

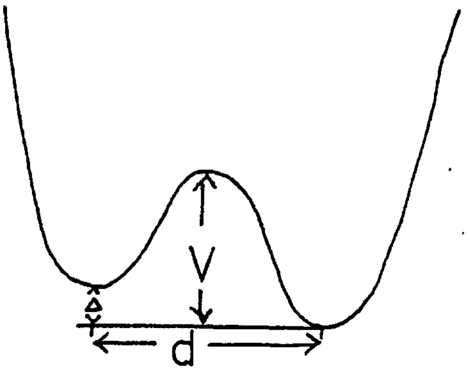


Figure 1.2

Part of the potential energy surface of a glass, producing a tunnelling state with barrier V, asymmetry energy Δ and generalized distance d.

CHAPTER 2

LINE DEFECTS AND THE GLASS TRANSITION

2.1 Introduction

One of the striking features of glass forming liquids is the functional form of the temperature dependence of a number of transport properties, in the supercooled regime. The viscosity, diffusion rate, nuclear spin relaxation rate all follow an empirical law (known as the Vogel-Fulcher law) which diverges as exp $\frac{A}{T-To}$ at a finite temperature (To). The universality of this behaviour, which is found in a wide variety of materials, implies that all relaxation properties of supercooled liquids are dominated by a common mechanism.

The work in this chapter is based on a suggestion by Anderson (1979) that such behaviour might be explained in terms of a defect dominated relaxation process. Using homotopy theory we demonstrate that line defects, characterized by the group of integers modulo two (Z_2), are the only stable excitations in amorphous media. From the general properties of such defects the temperature dependence of the density of defects is calculated, and this can be directly related to the average relaxation time of the medium. Such a procedure leads directly to a derivation of the Vogel

Fulcher law for the relaxation time of supercooled liquids.

2.2 The Classification of Defects in Ordered Media

In 1976 Toulouse and Kleman introduced a scheme in which a branch of algebraic topology, known as homotopy theory, is used to classify the topologically stable defects in ordered media. The starting point is a field, or order parameter, ($\phi(\underline{x})$) which is a function of the spacial co-ordinates of the medium ($\underline{x}$). In mathematical language the field defines a mapping from the real space of the medium (Σ) to the manifold of internal states (M).

i.e. $\phi : \Sigma \rightarrow M$

If G is the symmetry group of the Lagrangian and H is the subgroup of G which leaves the ground state invariant, then M is the coset space G/H and it characterizes all possible ground states. In general the points of M have a one to one correspondence with the minima of the potential energy surface. The mapping is such that we expect the order parameter at every point to reside in the potential energy minimum, but spacial variations may increase the global energy.

Topological defects are singularities which can be detected from the configuration of the field on a surface surrounding the defect. The field maps closed n-dimensional surfaces (n-spheres) of the medium onto closed surfaces in the Manifold of Internal States and these n-surfaces fall naturally into equivalence classes which make up the n-th homotopy group of M, $\Pi_n(M)$. Surfaces are equivalent if they can be continuously deformed into each other within the Manifold and the set of all equivalent n-surfaces constitutes one element of the n-th Homotopy group. The identity element of the group is the set of all surfaces which can be continuously shrunk to zero.

To see how this relates to defects we consider the specific example of the mapping of a closed path (one dimensional surface) onto a closed path in the Manifold of internal states. If the latter contour cannot be shrunk continuously (it belongs to a nontrivial element of the first homotopy group) whereas the real space contour can, then on shrinking the real space contour a situation is reached where an infinitesimal path in Σ maps onto a finite path in M. Such a contour must enclose a singularity of the field, that is a point where the mapping is not defined. The locus of the singularity in a medium (of dimensionality greater than two) is an uninterrupted line because any procedure for shrinking the contour must encounter it.

In general, defects of dimensionality r are classified by the nth Homotopy group in d spacial dimensions where

$$n = d - r - 1$$

Thus any defect can be characterized by the homotopy class of the mapping of a surface surrounding it and, by definition, a defect cannot be continuously deformed from one class to another. Defects combine according to the addition law of the corresponding Homotopy group.

2.3 Classification of Defects in Amorphous Media

The generalization of the above approach to disordered media is straight forward (Toulouse 1979, Rivier 1979) but a careful interpretation of the results is required. The "ground state" of a glass has no constructive symmetry thus H is trivial ($H = \mathbb{1}$) and $M = G/H = G$ the Euclidean group. The following points must, however, be considered:-

(i) Is it reasonable to define an order parameter in a medium without order?

(ii) The potential energy surface of glasses is complicated and it would be futile to attempt to construct a manifold of internal states representing the minima of this surface.

In the method outlined below we define an order parameter by choosing a particular low energy ("ideal") configuration as a reference state for the actual configuration. Thus the manifold of internal states, for a particular reference configuration, is relevant to a restricted part of the potential energy surface. Homotopy theory is a valid method for classifying the stable singularities of any field theory and thus the problem is really that of finding a suitable field to represent the glassy state. By analogy with ordered media the "ground state" configuration should be represented by a uniform field, free from singularities. The ground state of a glass is not unique, but there are a number of deep minima in the potential energy surface which are separated from each other by large energy barriers. Thus for any glass at a reasonable temperature the corresponding minimum energy configuration is well defined and this configuration is considered to be the reference state in which the field maps every element of space into the identity of the manifold of internal states. Each element contains a macroscopic number of atoms and has no internal symmetry so the relevant group of transformations is the full rotation group (SO(3)). A continuous field theory can now be developed by considering the operation which transforms each group of atoms in an excited (or actual) state of the system to their configuration in the corresponding relaxed (reference) state. Small deviations in the detailed structure within a group of atoms are neglected.

The topologically stable singularities of this field theory are classified by the homotopy groups of the Rotation group:-

$$\Pi_1\ (SO(3)) = Z_2$$

$$\Pi_2\ (SO(3)) = \mathbb{1}$$

$$\Pi_3\ (SO(3)) = Z$$

The third Homotopy group does not label localized singularities, but rather nontrivial, nonsingular configurations of the whole system. They play an important role in high energy physics where they are singularities (called instantons) in four dimensional space-time. The second homotopy group is trivial, hence point defects are not topologically stable excitations in glasses. The first homotopy group is the group of integers modulo two (Z_2) thus one type of line defect is stable in glasses and the combination of any two defects will annihilate both (1+1=0).

The stability of line defects in these systems is due to the fact that the rotation group is not simply connected. A rotation of 2Π cannot be continuously deformed to the identity, whereas a rotation of 4Π can. The manifold of internal states can be represented by a solid, 3 dimensional sphere of radius Π, with the opposite points identified (Pollard 1976). The direction of the vector joining the centre of the sphere to a point of the manifold represents the axis of rotation ($\hat{n}$) and the magnitude of the vector represents the rotation angle (θ). For rotations of Π (represented by points on the surface of the sphere) rotations about an axis ($\hat{n}$) are equivalent to rotations about the opposite axis ($-\hat{n}$) thus opposite points on the surface must be identified. Any closed contour crossing the surface of this manifold an even (odd) number of times can (cannot) be shrunk continuously to zero (Fig. 2.1).

Thus we see that the only topologically stable defects in amorphous materials are Z_2 line defects, associated with a rotation of the field by 2Π (about any axis) along a contour surrounding the line. Topological stability is not, however, equivalent to energetic stability. Defects belonging to the trivial element of the homotopy group may be prevented from decaying instantaneously by the presence of small energy barriers. Such a situation would account for the fact that dislocations like configurations appear to be stable against local perturbations in some models of amorphous metals (Chaudari, Levi and Steinhart 1979). A topologically stable defect can either decay by combination with another defect or by tunnelling through (or activation over) large energy barriers associated with the departure of the field from the manifold of internal states (and from the potential energy minimum). A closed line defect can be eliminated by inducing a singularity of the field on a plane bounded by the defect (see, for example, figure 2.2) in the intermediate state. Thus, in general, the energy barriers and average life time associated with topologically stable defects are much longer than those of topologically trivial "defects".

2.4 Relaxation in Supercooled Liquids

As the glass transition of a supercooled liquid is approached, it is generally found that the relaxation times associated with all the relaxation properties (viscosity, self diffusion, nuclear spin relaxation rate) increase very rapidly with a universal law known as the Vogel-Fulcher law:

$$t = to \quad \exp \frac{A}{T-To} \qquad 2.1$$

The constants A and To are the same for all properties of a given material. The functional form of this law is unusual in that it has an essential singularity at a finite temperature (To) which is of the order of 10-100°K below the glass transition temperature (Tg). It cannot be derived from the more usual Arrhenius behaviour (corresponding to To = 0) by invoking any reasonable distribution of energy barriers. The universal form of the law suggests that all relaxation processes in supercooled liquids are dominated by a single mechanism. The transport properties of crystals are, in general, dominated by the presence of defects (plastic flow occurs via dislocations and diffusion via vacancies). Here we consider the possibility that the line defects discussed in the previous section might explain the unusual temperature dependence of the relaxation time in supercooled liquids.

The argument is based on the Glarum model for relaxation in liquids (Glarum 1960, Phillips, Barlow and Lamb 1972). The basic assumption of the model is that structural relaxation of a group of atoms or molecules cannot occur until a defect has succeeded in diffusing to the site of that group. The presence of a defect core distorts the structure to such a degree that the transition to the lower energy configuration is easily achieved. The defects must be stable entities, with average lifetimes longer than the timescales under consideration, thus the arguments are not applicable to defects which are not topologically stable (for example free volume). Assuming that diffusion occurs via a random walk process, the average time necessary for a defect to diffuse to a given site is proportional to the square of the distance between them. Dimensional analysis suggests that the average distance between a site and the nearest defect is inversely proportional to the square root of the density of defects ρ (the total length of defect line per unit volume). Thus the average relaxation time $\bar{t}$ is inversely proportional to the density of defects in the medium

$$\text{i.e} \quad \bar{t} \; \alpha \; \bar{d}^2 \; \alpha \; \rho^{-1} \qquad 2.2$$

2.5 Equilibrium Density of Line Defects

The density of defects in equilibrium (ρ eq) at a given temperature is found by minimizing the free energy with respect of ρ.

$$F(\rho) = E(\rho) - TS(\rho) \qquad 2.3$$

$$\left.\frac{\partial F(\rho)}{\partial \rho}\right|_{\rho eq} = 0 \qquad 2.4$$

Here $S(\rho)$ is the contribution to the entropy by a defect density ρ and $E(\rho)$ is the corresponding energy contribution.

2.5.1 Entropy of Line Defects

The configurational entropy of line defects is, in general, a difficult problem but by introducing a number of approximations we can obtain an expression which is valid for low defect concentrations. We consider a network of F faces which can be occupied by closed defect lines (threading through the defective faces) of total length Na, where a is the step length of the order of the interatomic distance. Then

$$\rho = \frac{Na}{\gamma F a^3} \qquad 2.5$$

γ is a numerical factor relating the number of faces to the volume. The total number of configurations (Ω_N) in such a situation (assuming $1 \ll N \ll F$) is given by:-

$$\Omega_N = \sum_{\ell=1}^{\ell max} \binom{F}{\ell} \sum_{n_1=n_0}^{N} \sum_{n_2=n_0}^{N} \sum_{n_\ell=n_0}^{N} \frac{C(n_1)}{n_1} \frac{C(n_2)}{n_2} \cdots \frac{C(n_\ell)}{n_\ell} \delta(\sum_{i=1}^{\ell} n_i - n) \qquad 2.6$$

Here the combinational factor counts the possible starting positions of the ℓ loops. The second summation partitions the ℓ loops with N total steps into n_1, $n_2 \ldots n_\ell$ steps respectively. A loop with n_i steps has $C(n_i)$ configurations, the number of self avoiding closed walks of n_i steps. The factor $\frac{1}{n_i}$ is included because of the n_i equivalent starting points. For $N \ll F$ the exclusion of faces already occupied by previous loops yields a negligible correction. The precise form of C(n) is unknown but, by analogy with a well tested scaling law for self avoiding walks (Domb 1969) we can write:-

$$\frac{C(n)}{n} = K \; n^{-\beta} \; \zeta^n \qquad 2.7$$

Here ζ is of the order of the connectivity of the network (Z-1), $\beta \sim \frac{11}{4}$ and $K \sim \frac{1}{2}$. This expression is strictly valid for large n but, as we shall see, for small n the precise form of C(n) is unimportant.

Defining a generating function for a single loop.

$$f(x) = \sum_{p=n_0}^{\infty} \frac{x^p}{p^\beta} \qquad 2.8$$

where n_o is the number of steps in the smallest possible loop, then

$$\sum_{n_1=n_0}^{N} \cdots \sum_{n_\ell=n_0}^{N} \delta(\Sigma n_i - N)\frac{1}{n_1\beta}\,\frac{1}{n_2\beta}\cdots\frac{1}{n_\ell\beta} = \frac{1}{N!}\left(\frac{\partial}{\partial x}\right)^N [f(x)]^\ell \Big|_{x=o} \qquad 2.9$$

and

$$\Omega_N = \frac{\zeta^N}{N!}\left\{\left(\frac{\partial}{\partial x}\right)^N \sum_{\ell=1}^{\ell max} \frac{F!}{(F-\ell)!\,\ell!} K^\ell [f(x)]^\ell\right\} \Big|_{x=o} \qquad 2.10$$

The lowest order term of $[f(x)]^\ell$ is $x^{\ell no}$ thus for $\ell > \ell max$ (the integral part of $\frac{N}{n_o}$)

$\left(\frac{\partial}{\partial x}\right)^N x^{\ell no} \Big|_{x=o} = 0$ and terms with $\ell > \ell max$ do not contribute to the sum. We can replace ℓmax by infinity without affecting the result. The sum is then a binomial expansion of the expression $(1+Kf(x))^F$

and $$\Omega_N = \frac{\zeta^N}{N!}\left\{\left(\frac{\partial}{\partial x}\right)^N [(1+Kf(x))^F - 1]\right\} \Big|_{x=o} \qquad 2.11$$

$$\simeq \frac{\zeta^N}{N!}\left\{\left(\frac{\partial}{\partial x}\right)^N [e^{FKf(x)} - 1]\right\} \Big|_{x=o} \qquad 2.12$$

Using $\lim_{s\to\infty} (1+\frac{a}{s})^s = e^a$

Expanding the exponential we have

$$\Omega_N = \frac{\zeta^N}{N!}\left\{\sum_{r=1}^{\infty} \frac{(FK)^r}{r!}\left(\frac{\partial}{\partial x}\right)^N f^r(x)\right\} \Big|_{x=o} \qquad 2.13$$

But $$\left(\frac{\partial}{\partial x}\right)^N f^r(x)\Big|_{x=o} = \left(\frac{\partial}{\partial x}\right)^N \left(\sum_{p=n_o}^{\alpha} \frac{x^p}{p\beta}\right)^r \Big|_{x=o}$$

$$= \left(\frac{\partial}{\partial x}\right)^N \left(\frac{x^{n_o r}}{n_o{}^{\beta r}} + 0(x^{n_o r+1})\right)\Big|_{x=o}$$

and the highest power of r to survive in this expression is

ℓ_{max}

$$\Omega_N = F^{\ell max} \left(\frac{\zeta^N}{N!} \, \frac{K}{n_o \beta \ell max}^{\ell max} \, \frac{N!}{\ell max!} + 0\,(F^{-1})\right). \qquad 2.14$$

But $\ell_{max} = \frac{N}{n_o} \left(1 + 0\left(\frac{n_o}{N}\right)\right)$

so for $N >> n_o$ we can neglect the non-integral part and set $\ell_{max} = \frac{N}{n_o}$

Then $$\Omega_N = \frac{(KF)^{N/n_o} \dots \zeta^N}{n_o^{N\beta/no} \left(\frac{N}{n_o}\right)!} \qquad 2.15$$

and $$\ln \Omega_N = N \ln \zeta - \left(\frac{N}{n_o} \ln \frac{N}{n_o} - \frac{N}{n_o}\right) + \frac{N}{n_o} (\ln K + \ln F)$$

$$- \frac{\beta}{n_o} N \ln n_o \qquad 2.16$$

$$= \frac{N}{n_o} (n_o \ln \zeta + 1 + \ln K - (\beta-1) \ln n_o) - \frac{N}{n_o} \ln \frac{N}{F} \qquad 2.17$$

The entropy per unit volume (S) is given by

$$S = k_B \frac{1}{\gamma a^3} \frac{\ln \Omega}{F}$$

or $$S = \frac{k_B}{a} (D\rho - C\rho \ln \rho a^2) \qquad 2.18$$

where $\rho = \frac{N}{\gamma F a^2}$ as above

$$C = \frac{1}{n_o} \qquad 2.19$$

$$D = \ln \zeta - \frac{1}{n_o} \ln \frac{\gamma no^{\beta-1}}{Ke} \qquad 2.20$$

The number of unknown parameters makes a numerical estimate of these constants unobtainable, however D is logarithmic in the geometrical parameters (K, γ, ζ) and so it depends only weakly on the detailed structure of the medium. In any case we are particularly interested in the functional form of the expression.

The physical interpretation of the above result is that when a given total length of defect is free to distribute among loops of any size, the entropy is dominated by the mixing entropy of the smallest possible loops, (which is of the order of $\ln N! \sim N \ln N$). Here we have considered only the configurational entropy of the defects, however their presence will affect the vibrational modes of the medium and so they must also contribute to the vibrational entropy. For free defects this effect should be small and we can absorb it into the linear term (D) in equation 2.18 (see for example Nabarro p.689).

2.5.2 Energy of Line Defects

The energy of line defects is calculated for a specific field theory of glass in chapter 3 of this thesis but in this chapter we approach the problem by analogy with the properties of defects in ordered media. In fact the results are equivalent for a particular range of defect concentration (the semi dilute regime).

In general, topological line defects in ordered media are associated with a distortion field which decreases as the inverse of the distance from the line. A transparent example is that of vortices in superfluid liquid Helium in which the order parameter is a complex wavefunction $\Psi = |\Psi| e^{i\Phi}$. In the equilibrium the modulus of the wavefunction $|\Psi|$ assumes a constant value, minimizing the potential energy, but the phase Φ is arbitrary. Under these conditions, the only remaining term in the free energy is $F_{Grad} = \int (\underline{\nabla}\Phi)^2 dV$. The wavefunction must be single valued thus

$$\oint \underline{\nabla} \Phi \, d\underline{l} = 2\Pi n$$

for any closed contour and the integer n is the topological invariant of the singular line enclosed by the contour. For a straight defect a circular contour of radius r, centred on the line has a length $2\Pi r$ thus, from axial symmetry, $\nabla \Phi = \frac{2\Pi n}{2\Pi r} = \frac{n}{r}$. The Euler Lagrange Equation is

$$\nabla^2 \Phi = \sum_i \lambda_i \, \delta^2(\underline{x} - \underline{\ell}i) \qquad 2.19$$

where i labels the defect lines. The two dimensional δfn is included because $\nabla\Phi$ is not defined on the core of the defect. The solution of this differential equation (with the boundary condition $\Phi = 0$ at infinity) is

$$\Phi(\underline{x}) = \sum_i \int \frac{\lambda_i \, \delta(\underline{x}^1 - \underline{\ell}i) \, d^3\underline{x}^1}{|\underline{x} - \underline{x}^1|} \qquad 2.20$$

Integrating F_{Grad} by parts and once again setting $\phi = 0$ at infinity leads to:-

$$F_{Grad} = \int \Phi \nabla^2 \Phi \, dV$$
$$= \sum_{i,j} \int\int \lambda_i \lambda_j \frac{d\ell i \; d\ell j}{|\underline{x}_i - \underline{x}j|} \qquad 2.21$$

An expression of this form is found for the interaction energy of many types of defect, vortices in liquids (Lamb 1932) and x-y ferromagnets, disclination lines in liquid crystals (De Gennes 1974) and, in a more complicated form, dislocations in crystals (Nabarro 1967). It is easily recognized as the Biot-Savart law for the interaction energy of current loops.

The above discussion is only strictly valid for defects labelled by the full group of integers(Z)(Dzyaloshinskii 1980), however Equation 2.21 is an upper limit for the interaction energy and it is correct for straight parallel defects. In the next chapter we demonstrate that the non abelian field theory necessary to describe such non algebraic defects reduces to an abelian (linear) theory in a particular concentration regime and the interaction energy is again described by equation 2.21.

The energy of a single straight defect line is logarithmic in the size of the system but the presence of a second (antiparallel) line screens the distortion field of the first and the size of the system is replaced by the distance between the defects. In fact for all loop geometries the interaction energy can be written, approximately as

$$E_N = Xa \sum_{i=1}^{N} \ln \frac{ri}{a} + N\, E_{core} \qquad 2.22$$

Here the line is split into N segments of length a and r_i is the distance between the ith segment and the nearest antiparallel one, the direction being determined by the orientation of the distortion field around the line. E_{core} is the core energy and x is a measure of the energy scale of the distortion (of the order of $\mu a^2/4\Pi$ where μ is the shear modulus).

For a random configuration of defect loops, equation 2.20 should be averaged over a probability distribution P(r) of the distance r. We are interested in the regime in which the defect concentration is high enough to introduce interaction between the defect loops, but low enough for the mutually avoiding potential in the entropy calculation (equation 2.6) to be neglected. In this (semi-dilute) regime the only length scale (ζ) in the problem is the average distance between the defect lines and is related to the density of defects (ρ) by

$$\zeta = \rho^{-\frac{1}{2}} \qquad 2.23$$

Thus the distribution function P(r) depends only on the distribution function ($\overline{P}(y)$) of the dimensionless parameter ($y = \frac{r}{\zeta}$)

$$P(r)\,dr = \overline{P}(\frac{r}{\zeta})\,d\,(\frac{r}{\zeta}) \qquad 2.24$$

and $$\left< \sum_{i=1}^{N} \ln \frac{r_i}{a} \right> = \int_0^\infty P(r) \ln \frac{r}{a} \, dr$$

$$= \int_0^\infty \overline{P}(y) \left(\ln y + \ln \frac{\zeta}{a}\right) dy$$

$$= N < \ln y > - \tfrac{1}{2} N \ln \rho a^2 \tag{2.25}$$

where $\int_0^\infty P(r)\, dr = \int_0^\infty \overline{P}(y)\, dy = N$

and $< \ln y > = \frac{1}{N} \int dy\, \overline{P}(y) \ln y$

Equation 2.22 becomes

$$E_N = Xa\, N(<\ln y > - \tfrac{1}{2} \ln \rho a^2) + N\, E_{core} \tag{2.26}$$

and the energy per unit volume of a defect density ($\rho = \frac{Na}{V}$) is

$$E(\rho) = \frac{B}{a} \rho - \frac{A}{a} \rho \ln \rho a^2 \tag{2.27}$$

with

$$A = \frac{Xa}{2} \tag{2.28}$$

$$B = a\, X < \ln y > + E_{core} \tag{2.29}$$

and the expression for the energy density has a similar form to that of the entropy density (2.18) in the semi dilute regime. Misushima (1960) used a similar expression for the energy of a large number of dislocation lines in a crystalline medium.

2.5.3 Equilibrium Density of Defects

Substituting equations 2.18 and 2.27 into the expression for the free energy density (2.3) we obtain:

$$F(\rho) = \frac{1}{a}(Ck_B T-A)\rho \ \ln\rho a^2 + \frac{1}{a}(B-Dk_BT)\rho \qquad 2.30$$

$$\text{and } \frac{\partial F(\rho)}{\partial \rho} = \frac{1}{a}(Ck_BT-A)\ \ln\rho a^2 + \frac{1}{a}(Ck_BT-A+B-Dk_BT) \qquad 2.31$$

$$\text{therefore } \rho^{eq} = \frac{1}{a^2} \exp - \frac{B-A+(C-D)k_BT}{Ck_BT-A} \qquad 2.32$$

$$= \alpha \exp - \frac{\beta}{T-To} \qquad 2.33$$

$$\text{with} \quad \alpha = \frac{1}{a^2} \exp \left(\frac{D}{C} - 1\right) \qquad 2.34$$

$$\beta = \frac{1}{k_BC}\left(B - \frac{AD}{C}\right) \qquad 2.35$$

$$To = \frac{A}{k_BC} \qquad 2.36$$

Thus the equilibrium density of defects falls continuously, but rapidly, *to zero at a finite temperature* To. The defect diffusion model for relaxation implies that the relaxation time associated with the transport properties is inversely proportional to the density of defects hence this timescale diverges at To and follows the observed Vogel-Fulcher law.

$$t \ \alpha \ \ \rho eq^{-1} = \alpha \exp \frac{\beta}{T-To}$$

The expression for the equilibrium density is only valid in the semi dilute regime as, when the defect concentration is very dilute, the small defect loops screen their own energy and do not interact with surrounding loops. In the concentrated limit the entropy expression becomes inaccurate because the defects were not considered to be mutually avoiding.

Experimentally the Vogel-Fulcher law is observed over a limited temperature range. At high temperature an Arrhennius behaviour is observed which suggests that structural relaxation occurs via an activation process in this regime, so clearly the molecules do not wait for defects to diffuse to them. Close to To the relaxation time becomes so long that measurements are difficult to obtain. The theory does imply, however, that the Fulcher law may break down before the infinite relaxation time is reached, thus the interpretation of To as the true glass transition temperature is suspect.

2.6 The Kauzmann Paradox

The temperature dependence of the entropy of a supercooled liquid is such that, were it possible to maintain the system in internal equilibrium (by avoiding the glass transition) the entropy of the liquid would, at a finite temperature (To), become equal to the entropy of the corresponding crystal (Fig. 1.1). This paradoxical situation was first noted by Kauzmann (1948). It lead to the suggestion (Gibbs, DiMarzio 1958) that a supercooled liquid would undergo a true second order phase transition, associated with a discontinuity in the temperature derivative of the entropy, at To. Adams and Gibbs (1965) used the assumption that the excess entropy increases linearly above To ($S_{ex} = A(T-To)$) to explain the functional form of the Vogel-Fulcher law.

Here, by attributing the excess entropy of the liquid to the topological defects, we show that this entropy tends to zero smoothly at a finite temperature To, without the discontinuity of the slope which would be present in a second order phase transition. Substituting the expression for the equilibrium density of defects (2.33) into the entropy equation (2.18) we find:

$$S(T) = \frac{k_B}{a}\,(D\rho_{eq}(T) - C\rho_{eq}(T)\,\ln\rho_{eq}(T)) \qquad 2.37$$

$$= \frac{k_B}{a}\,(\alpha \exp - \frac{\beta}{T-To})(D - C(\ln\alpha a^2 - \frac{\beta}{T-To})) \qquad 2.38$$

$$= \frac{k_B}{a}\,\alpha(\exp - \frac{\beta}{T-To})(C + \frac{C\beta}{T-To}) \qquad 2.39$$

Thus $\lim\limits_{T \to To} S(T) = \lim\limits_{T \to To} \frac{Ck_B\alpha}{a} \; \frac{1}{T-To} \exp - (\frac{\beta}{T-To})$

$= 0$

and $\lim\limits_{T \to To} \frac{\partial S(T)}{\partial T} = \lim\limits_{T \to To} \frac{Ck_B\,\beta\alpha}{a} \left(- \frac{1}{(T-To)^2} + \frac{\beta}{(T-To)^3}\right) \exp - \frac{\beta}{T-To}$

$= 0$

In fact all higher temperature derivatives also tend to zero as T approaches To and thus the phase transition at To must be infinite order. However, close to To equation 2.33 is not valid (the defects are too few to interact as in equation 2.21) and therefore it is unlikely that any transition would occur at To, even in a liquid cooled slowly enough for internal equilibrium to be maintained down to this temperature.

2.7 Conclusions

In this chapter we discussed the application of homotopy theory to amorphous materials and showed that line defects, which are their own antidefects, are the only topologically stable singularities in these systems. The temperature dependence of the equilibrium density of such defects was calculated, and found to follow a Vogel-Fulcher law in the semi dilute regime. The assumption that structural relaxation occurs at a site only when a defect has succeeded in diffusing to that site leads directly to an explanation of the temperature dependence of the relaxation time observed in supercooled liquids. The entropy of the defects (and all the temperature derivatives of the entropy) tend to zero at a finite temperature, thus resolving the Kauzmann Paradox.

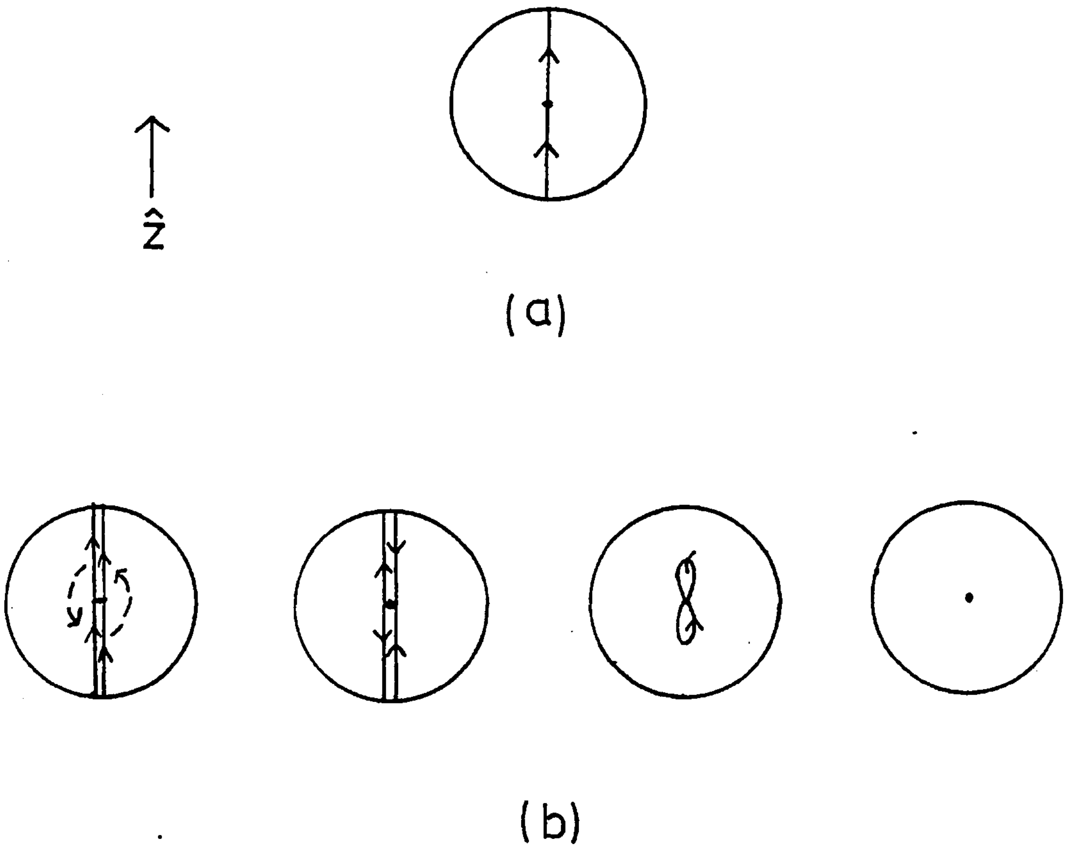


Figure 2.1

(a) Path in the manifold of internal states representing a rotation by 2π about the $\hat{Z}$ axis.

(b) Path representing a 4π rotation. The rotation of one half of the contour leads to a situation which can be shrunk continuously to zero.

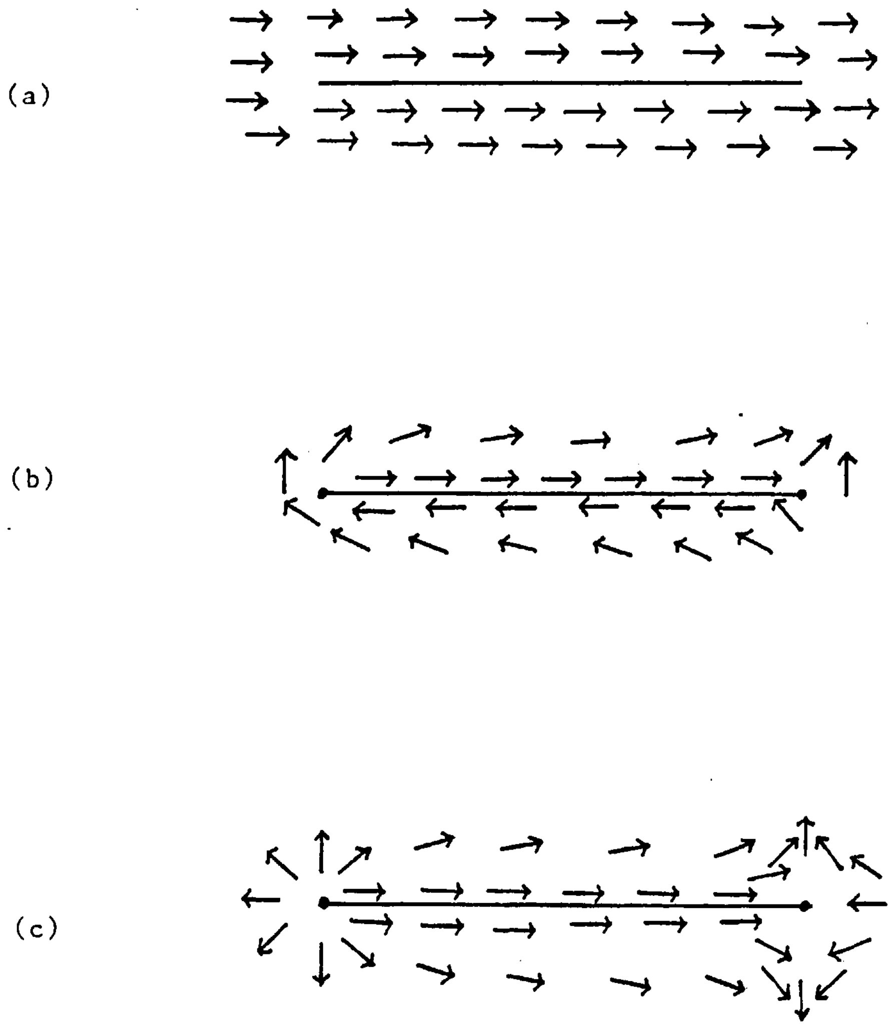


Figure 2.2

Excitation of a vortex loop in an x-y ferro-magnet

(a) Initial configuration.

(b) An Intermediate configuration with singular plane.

(c) 2Π vortex loop (cross section).

CHAPTER 3

A GAUGE INVARIANT FIELD THEORY OF GLASS

3.1 Introduction

In the previous chapter we discussed how one might expect to find topologically stable line defects, characterized by the group of integers modulo two, in all amorphous materials. In order to calculate the energy of such defects, and examine the low temperature properties of glass, we introduce a field theory in which the macroscopic homogeneity of the glassy state is formulated as a local invariance of the free energy. The line defects are singularities of the matter field which are, in some respects, analogous to vortices in type II superconductors.

The intrinsic defects of the discrete network underlying the continuum are included as punctures in an otherwise continuous space and the boundary conditions on these punctures are such that they act as sources of distortion. Associated with each defect are two distinct ground state configurations and the tunnelling rate between them is related to the size of the defect. Such tunnelling modes, or two level systems, lead directly to a distribution of split pairs of gauge invariant states which could be responsible for the linear specific heat and other low temperature anomalies of glasses.

3.2 The Gauge Invariant Free Energy

The concept of gauge invariance in a glass arises from the combination of the absence of symmetry and the overall homogeneity. There is no unique reference frame for the system as a whole, thus at every point the local reference frame is arbitrary and the physics cannot depend on which frame we choose. In other words the local orientation (phase) of the matter field (the local structure) is not an observable quantity, but the magnitude (the local density) is. Such a situation occurs in superconductivity where the local phase of the wavefunction is arbitrary but the amplitude is observable. However, in both cases, the relative orientation of the matter field at two difference points in space (phase difference) is, in principle, observable and this necessitates the introduction of a gauge field to counteract the effect of making an arbitrary change in the local reference frame at any point. Thus the physics (hence the energy) remains invariant under such a local transformation. The derivative in the expression for the free energy is replaced by a covariant derivative which is a combination of the ordinary derivative and the gauge field. In fact the gauge field plays the part of the connection in differential geometry and it compares the minimum energy configuration of the matter field at one point with that of a neighbouring point. Such a connection is always required in disordered systems because of the noncollinear nature of the ground state. Local invariance also implies that states of the system related to each other by a continuous gauge transformation are not distinct physical states, however those related by a nontrivial (discontinuous) gauge transformation are distinct, and the transition between two such states is mediated by tunnelling.

The idea of representing a disordered system by a gauge field theory in continuous space is not new. It has been introduced for spin glass but the problem of representing the quenched disorder has not been satisfactorily solved, either by quenching the gauge field (Hertz 1978) or by keeping it as a dynamical variable and assigning it, somewhat arbitrarily, a mass (Dzyaloskinskii and Volovik (1978)). Rivier (1980) and Da Silva (1980) also considered the gauge field to be a dynamical variable but quenched the frustration lines and expressed them as sources of curvature. Here we use a similar approach for glasses, but consider a nonabelian model in which the intrinsic defects are included as lines of quenched curvature.

From the above discussion it is evident that the free energy density describing a field theory of a glass must be invariant under local rotations.

The absence of symmetry implies that the group of transformations of the matter field ($\hat{\emptyset}(\underline{x})$) is the full rotation group (SO(3)) and as such $\hat{\emptyset}(\underline{x})$ can be represented by a 3 dimensional rank 2 tensor. A covariant derivative $\hat{D}\mu$ defined by

$$\hat{D}\mu = \partial\mu\mathbb{1} + g\,[\hat{A}\mu, \qquad 3.1$$

or explicitly $(\hat{D}\mu\hat{\emptyset})ij = \partial\mu\emptyset ij + g(A_{ik}\emptyset_{kj} - \emptyset_{ik}A_{kj})$ 3.2

is introduced and the gauge fields $\hat{A}\mu$ transform in such a way as to ensure that $\hat{D}\mu\hat{\emptyset}$ is covariant under local rotations ($\hat{U}(x) \varepsilon$ SO(3), $\hat{U}^+ = \hat{U}^{-1}$)

ie $D\mu\hat{\emptyset}(\underline{x})^1 = \partial\mu\hat{\emptyset}^1(\underline{x})^+ g\,[\hat{A}^1_\mu(\underline{x}), \hat{\emptyset}^1(\underline{x})] =$

$$\hat{U}(\underline{x})\ (D\mu\hat{\emptyset}(\underline{x}))\ \hat{U}^{-1}(\underline{x}) \qquad 3.3$$

where $\hat{\emptyset}^1(\underline{x}) = \hat{U}(\underline{x})\ \hat{\emptyset}(\underline{x}) \quad \hat{U}^{-1}(\underline{x})$ 3.4

We distinguish formally between directions in real space ($\mu = 1,2,3$) and directions in isospin space ($i,j = 1,2,3$). Summation over repeated indices is implied.

From equation 3.4 we see that

$$\partial\mu\hat{\emptyset}^1(\underline{x}) = \hat{U}(\partial_\mu\hat{\emptyset})\hat{U}^{-1} + (\partial\mu\hat{U})\hat{\emptyset}\hat{U}^{-1} + \hat{U}\hat{\emptyset}(\partial\mu\hat{U}^{-1}) \qquad 3.5$$

$$= \hat{U}(\partial\mu\hat{\emptyset})\hat{U}^{-1} - [\hat{U}\partial\mu\hat{U}^{-1},\ \hat{\emptyset}^1] \qquad 3.6$$

using the property $\hat{U}\partial_\mu\hat{U}^{-1} = -(\partial_\mu\hat{U})\hat{U}^{-1}$ 3.7

Now equation 3.3 becomes

$$\hat{U}(\partial_\mu\hat{\emptyset})\hat{U}^{-1} - [\hat{U}\partial_\mu\hat{U}^{-1}, \hat{\emptyset}^1] + g\,[\hat{A}^1_\mu, \hat{\emptyset}^1]$$

$$= \hat{U}(\partial_\mu\hat{\emptyset})\hat{U}^{-1} + g[\hat{U}\hat{A}_\mu\hat{U}^{-1}, \hat{\emptyset}^1]$$

therefore $\hat{A}^1_\mu = \hat{U}\hat{A}_\mu\hat{U}^{-1} + g^{-1}\hat{U}(\partial_\mu\hat{U}^{-1})$ 3.8

A gauge invariant free energy density $(f(\underline{x}))$, with the coupling between the matter field and the gauge field being effected solely through the covariant derivative (minimal coupling), can now be constructed.

$$f(\underline{x}) = \gamma(\hat{D}_\mu\hat{\phi}(\underline{x}))^{ij}(\hat{D}_\mu\hat{\phi}(\underline{x}))^{ij} + \hat{F}^{ij}_{\mu\nu}\hat{F}^{ij}_{\mu\nu} + U(\hat{\phi}(\underline{x})) \qquad 3.9$$

The potential $U(\hat{\phi})$ is a linear combination of the invariants of the matter field, up to order ϕ^4.

$$U(\hat{\phi}) = \alpha\phi^{ij}\phi^{ij} + \beta_1(\phi^{ij}\phi^{ij})^2 + \beta_2(\phi^{ij}\phi^{il}\phi^{kj}\phi^{kl}) \qquad 3.10$$

$$= \alpha\mathrm{Tr}(\phi\phi^T) + \beta_1(\mathrm{Tr}\phi\phi^T)^2 + \beta_2\mathrm{Tr}(\phi\phi^T\phi\phi^T) \qquad 3.11$$

$\gamma\ \beta_1\beta_2(>o)$ and $\alpha(<o)$ are constants.

The curvature tensor $\hat{F}_{\mu\nu}$ is the lowest order function of the gauge fields which is covariant under local rotations. It is, in fact, the nonabelian generalization of the magnetic induction of electromagnetism.

$$\hat{F}_{\mu\nu} = \partial_\mu\hat{A}_\nu - \partial_\nu\hat{A}_\mu + g\,[\hat{A}_\mu, \hat{A}_\nu] \qquad 3.12$$

$$\hat{F}'_{\mu\nu} = \partial_\mu\hat{A}'_\nu - \partial_\nu\hat{A}'_\mu + g\,[\hat{A}'_\mu, \hat{A}'_\nu]$$

$$= \partial_\mu[\hat{U}\hat{A}_\nu\hat{U}^{-1} + g^{-1}\hat{U}\partial_\nu\hat{U}^{-1}] - \partial_\mu[\hat{U}\hat{A}_\mu\hat{U}^{-1} + g^{-1}\hat{U}\partial_\mu\hat{U}^{-1}]$$

$$+ g\{[\hat{U}\hat{A}_\mu\hat{U}^{-1} + g^{-1}\hat{U}\partial_\mu\hat{U}^{-1}][\hat{U}\hat{A}_\nu\hat{U}^{-1} + g^{-1}\hat{U}\partial_\nu\hat{U}^{-1}]$$

$$- [\hat{U}\hat{A}_\nu\hat{U}^{-1} + g^{-1}\hat{U}\partial_\nu\hat{U}^{-1}]\ [\hat{U}\hat{A}_\mu\hat{U}^{-1} + g^{-1}\hat{U}\partial_\mu\hat{U}^{-1}]\}$$

$$= \hat{U}\,(\partial_\mu\hat{A}_\nu - \partial_\nu\hat{A}_\mu + g[\hat{A}_\mu, \hat{A}_\nu])\,\hat{U}^{-1}$$

$$= \hat{U}\,\hat{F}_{\mu\nu}\,\hat{U}^{-1} \qquad 3.13$$

The gauge fields $\hat{A}_\mu$ can be written as linear combinations of the generators of the rotation group (antisymmetric tensors) therefore

$$A^{ij}_\mu = -A^{ji}_\mu \qquad 3.14$$

We can define the dual (isospin) vectors $(\underline{A}_\mu)$, by

$$A^k_\mu = \tfrac{1}{2}c^{ijk}\,A^{ij}_\mu \qquad 3.15$$

and the covariant derivative in terms of these vectors becomes $[D\mu\hat{\emptyset}]^{ij} = \partial\mu\emptyset^{ij} + g\,(\epsilon^{ilk}\,A^k_\mu\,\emptyset^{lj} - \epsilon^{ljk}\,A^k{}_\mu\emptyset^{il})$

3.16

The Euler Lagrange Equations for the free energy ($F = \int f(\underline{x})\,d\underline{x}$) obtained by minimizing with respect to $\emptyset_{ij}$ and A^k_μ respectively are:

$$\gamma\,[\hat{D}\mu\;\hat{D}\mu\;\hat{\emptyset}]^{ij} = \frac{\partial U(\emptyset)}{\partial\emptyset^{ij}} \qquad 3.17$$

and $$\epsilon^{ijk}\{[\hat{D}\mu\;\hat{F}\mu\upsilon]^{ij} - \gamma g[\hat{D}\upsilon\;\hat{\emptyset},\;\hat{\emptyset}^T]^{ij}\} = 0 \qquad 3.18$$

In the remainder of this chapter we confine our attention to field configurations $\{\bar{\emptyset}\}$ which lie in the minimum of the potential energy surface everywhere, except close to defect cores.

i.e $$\frac{\partial U}{\partial\emptyset_{ij}}\Bigg|_{\bar{\emptyset}^{ij}} = \bar{\emptyset}^{ij}\,(4(\bar{\emptyset}^{ki}\,\bar{\emptyset}^{kl})\,\beta_1 + 2\alpha) + 4\beta_2\,\bar{\emptyset}^{ik}\,\bar{\emptyset}^{lk}\,\bar{\emptyset}^{lj} = 0 \qquad 3.19$$

This condition can be satisfied by choosing $\bar{\emptyset}$ to be proportional to a real rotation matrix $\hat{\Omega}$ $(\hat{\Omega}\,\hat{\Omega}^T = \mathbb{1})$

$$\bar{\emptyset} = \lambda\hat{\Omega} \qquad 3.20$$

and λ is a scalar measure of the "size" of the matter field. Equation 3.19 becomes $(\alpha + 6\beta_1\,\lambda^2 + 2\beta_2\,\lambda^2)\Omega^{ij} = 0$

or $$\lambda^2 = -\frac{\alpha}{2\beta_2 + 6\beta_1} \equiv \lambda_o{}^2 \qquad 3.21$$

and $$\begin{aligned} U\text{min} &= 3\,\alpha\,\lambda_o{}^2 + 9\beta_1\,\lambda_o{}^4 + 3\beta_2\lambda_o{}^4 \\ &= -\frac{\alpha^2}{4(3\beta_1 + \beta_2)} \end{aligned} \qquad 3.22$$

We now redefine the zero of the energy scale such that $U \rightarrow U + \dfrac{\alpha^2}{4(3\beta_1+\beta_2)}$ and $U(\lambda\hat{\Omega}) = U\min = 0$

Thus we consider the situation where the matter field has zero potential energy everywhere in the space Σ. We must exclude from this space all regions for which the matter field is not well defined, such as the cores of defects. Hence the space Σ is punctured and boundary conditions must be imposed on the surface of these punctures which reflect the character of the defect within them. In Σ, however, the field can be represented everywhere by a rotation matrix $\hat{\Omega}$ and an infinitesimal phase operation $\hat{\mathcal{A}}\mu$, representing the difference in the orientation of the matter field at the two points ($\underline{x}$ and $\underline{x} + d\underline{x}\,\mu$), is defined as follows:

$$\partial\mu\hat{\Omega}(\underline{x}) = [\hat{\mathcal{A}}\mu,\ \hat{\Omega}(\underline{x})] \qquad 3.23$$

with the solution,

$$\hat{\Omega}(\underline{x}) = (Ps \exp \int_{\underline{x}_o}^{\underline{x}} dx_\mu\ \hat{\mathcal{A}}_\mu(\underline{x}))\,\Omega_o(\bar{P}s \exp -\int_{\underline{x}}^{x_o} dx_\mu \hat{\mathcal{A}}_\mu(\underline{x})) \qquad 3.24$$

Ps is the path ordering operator, ordering the integral along the path from $\underline{x}o$ (the point at which the matter field is Ω_o) to $\underline{x}$. $\bar{P}s$ orders the integral along the reversed path. The matter field ($\underline{x}$) is path independent if and only if there exists an operator $\hat{W}(\underline{x}) \in SO(3)$ for all $\underline{x}$, such that

$$\hat{\mathcal{A}}_\mu(\underline{x}) = [\partial\mu\ \hat{W}(\underline{x})]\ \hat{W}^{-1}(\underline{x}) \qquad 3.25$$

then $\hat{\Omega}(\underline{x}) = \hat{W}(\underline{x})\ \Omega_o\ \hat{W}^{-1}(\underline{x})$ 3.26

and $\hat{W}(\underline{x}) = \mathrm{Ps}\ \exp \int_{\underline{x}_o}^{x} dx\mu\ \hat{\chi}^{\mu}\ (\underline{x})$ 3.27

$W(\underline{x})$ is the rotation of the matter field at a point $\underline{x}$ with respect to the orientation at some reference point $\underline{x}o$. The existence of a single valued function $(W(\underline{x}))$ defined by equation 3.25, implies that the curvature $(\hat{G}\mu\upsilon)$ associated with $\hat{\chi}_\mu$ vanishes everywhere.

$$\hat{G}\mu\upsilon(\underline{x}) = \partial\mu\hat{\chi}\upsilon(\underline{x}) - \partial\upsilon\hat{\chi}_\mu(\underline{x}) + [\hat{\chi}\mu,\ \hat{\chi}\upsilon] = 0 \qquad 3.28$$

The matter field is related to the state of the system and as such it must be uniquely defined at every point in the space Σ (it must be single valued) therefore equation 3.28 must hold everywhere, and $\hat{W}(\underline{x})$ is also uniquely defined at every point of space. For closed contours

$$\mathrm{Ps}\ \exp \oint dx\mu\ \hat{\chi}_\mu = \mathbb{1} \qquad 3.29$$

because the matter field must return to its initial configuration on completing a closed contour.

It is convenient to work in the rotated local reference frame in which any operator.. $\hat{\Lambda}(\underline{x})$ becomes

$$\tilde{\Lambda}(\underline{x}) = \hat{W}^{-1}(\underline{x})\ \hat{\Lambda}(\underline{x})\ \hat{W}(\underline{x}) \qquad 3.30$$

and
$$\begin{aligned}\tilde{D}\mu\ \tilde{\Lambda}(\underline{x}) &= \hat{W}^{-1}(\underline{x})\ \ \hat{D}\mu\ \hat{\Lambda}(\underline{x})\ \ \hat{W}(\underline{x}) \\ &= \partial_\mu(\hat{W}^{-1}\hat{\Lambda}\hat{W})-(\partial_\mu\hat{W}^{-1})\hat{\Lambda}\hat{W}-\hat{W}^{-1}\hat{\Lambda}(\partial_\mu\hat{W}) \\ &\qquad +g\ (\hat{W}^{-1}\hat{A}_\mu\ \hat{\Lambda}\ \hat{W} - \hat{W}^{-1}\ \ \hat{\Lambda}\ \hat{A}_\mu\hat{W})\end{aligned}$$

$$= \partial\mu\tilde{\Lambda} + \tilde{\gamma}_{\mu}\,\tilde{\Lambda} - \tilde{\Lambda}\tilde{\gamma}_{\mu} + g(\tilde{A}_{\mu}\tilde{\Lambda} - \tilde{\Lambda}\,\tilde{A}_{\mu})$$

$$= \partial\mu\tilde{\Lambda} + g[\tilde{A}_{\mu} + g^{-1}\tilde{\gamma}_{\mu}, \tilde{\Lambda}] \qquad 3.31$$

We define a new field

$$\tilde{C}_{\mu} = \tilde{A}_{\mu} + g^{-1}\,\tilde{\gamma}_{\mu} \qquad 3.32$$

which is, in effect, a combination of the gauge field and the phase gradient of the matter field. Such a combination is <u>invariant</u> under local rotations ($\hat{U}(\underline{x})$) because the matter field rotation is cancelled by the gauge field rotation:-

$$\hat{W}'(\underline{x}) = \hat{U}(\underline{x})\,\hat{W}(\underline{x}) \qquad 3.33$$

therefore $\tilde{\gamma}^{1}_{\mu} = \hat{W}^{-1}\hat{U}^{-1}(\partial\mu(\hat{U}\hat{W})\,\hat{W}^{-1}\hat{U}^{-1})\hat{U}\hat{W}$

$$= \hat{W}^{-1}\hat{U}^{-1}(\partial\mu\hat{U})\,\hat{W} + \hat{W}^{-1}(\partial\mu\hat{W})\hat{W}^{-1}\hat{W}$$

$$= \tilde{\gamma}_{\mu} + \hat{W}^{-1}\,(\hat{U}^{-1}\partial_{\mu}\hat{U})\hat{W} \qquad 3.34$$

and $\tilde{A}^{1}_{\mu} = \hat{W}^{-1}\hat{U}^{-1}(\hat{U}\hat{A}_{\mu}\hat{U}^{-1} + g^{-1}\,\hat{U}\partial_{\mu}\hat{U}^{-1})\hat{U}\hat{W}$

$$= \hat{W}^{-1}\hat{A}_{\mu}\hat{W} + g^{-1}\hat{W}^{-1}(\partial\mu\hat{U}^{-1})\,\hat{U}\,\hat{W}$$

$$= \tilde{A}_{\mu} - g^{-1}\hat{W}^{-1}(\hat{U}^{-1}\partial\mu\hat{U})\,\hat{W} \qquad 3.35$$

therefore $\tilde{C}^{1}_{\mu} = \tilde{C}_{\mu}$ $\qquad$ 3.36

The curvature of this field ($\tilde{F}\mu\upsilon$) is due to the gauge field curvature alone, since the matter field curvature is zero. Thus

$$\tilde{F}\mu\upsilon = \partial\mu\tilde{C}\upsilon - \partial\upsilon\tilde{C}\mu + g[\tilde{C}\mu, \tilde{C}\upsilon] \qquad 3.37$$

$$= \hat{W}^{-1}\hat{F}\mu\upsilon\,\hat{W} \qquad 3.38$$

The free energy density, itself gauge invariant, can be written in terms of the gauge invariant $\tilde{C}\mu$ fields.

$$f(\underline{x}) = \lambda_o^2\gamma \mathrm{Tr}[\hat{W}^{-1}(\hat{D}\mu\hat{\Omega})\hat{W})(\hat{W}^{-1}(\hat{D}\mu\hat{\Omega})\hat{W})^T]$$
$$+ \mathrm{Tr}[\hat{W}^{-1}\hat{F}\mu\upsilon\hat{W})(\hat{W}^{-1}\hat{F}\mu\upsilon\hat{W})^T] \qquad 3.39$$

$$=\lambda_o^2\gamma g^2 \mathrm{Tr}\{[\widetilde{C}\mu,\hat{\Omega}_o][\tilde{C}\mu,\hat{\Omega}_o]^T\} + \mathrm{Tr}\{\tilde{F}\mu\upsilon\ \tilde{F}^T_{\mu\upsilon}\} \qquad 3.40$$

and the corresponding Euler Lagrange equations are

$$\varepsilon^{ijk}\{[\tilde{D}\mu\ \tilde{F}\mu\upsilon]^{ij} - \gamma\lambda_o^2\ g^2\ [[\tilde{C}\nu,\hat{\Omega}_o],\hat{\Omega}_o^{-1}]^{ij}\} = 0 \qquad 3.41$$

(Using $\tilde{C} = -\tilde{C}^T$)

The classical ground or metastable states of the glass are given by the solutions of 3.41, subject to the boundary conditions on the punctures of Σ. Each configuration $\{\tilde{C}\mu\}$ corresponds to a continuous of configurations of the gauge field and the matter field $\{\tilde{A}\mu, \hat{\Omega}\}$, however, as we shall see in the next section, only those configurations which cannot be transformed into each other by continuous gauge transformations, are different physical ground states of the system.

3.3 Classification of Ground State Configurations

We are considering the situation where the matter field $(\lambda\ \hat{\Omega}\ (\underline{x}))$ has zero potential energy everywhere in Σ and thus we must exclude from Σ all regions of the space where this condition cannot be satisfied, or where $\hat{\Omega}\ (\underline{x})$ is not well defined. The origin of such regions in a glass is the structure of the discrete space underlying the continuum. Consider, for example, a spin glass model in which x-y or Heisenberg spins reside on a simple cubic lattice with random ferromagnetic and antiferromagnetic nearest neighbour interactions. As discussed in chapter 1, this model has intrinsic defects (frustration lines) which are the lines threading the elementary squares with an odd number of antiferromagnetic bonds (frustrated plaquettes). The spins on such a plaquette are necessarily distorted, because it is impossible to satisfy all bonds simultaneously, and the spin field is not well defined everywhere within the plaquette. This region must be excluded from any continuum model and, since the lines threading frustrated plaquettes in a 3 dimensional model must be continuous (Toulouse 1977), the holes are extended tubes, or punctures, which cannot end within the medium.

An alternative way of describing the same effect is that parallel transport of the spin around a frustrated plaquette (effected by minimizing the energy across each bond in turn) does not return the spin to its initial configuration. In field theory, parallel transport of a vector around a closed contour resulting in a finite rotation of the vector signals the presence of curvature within the contour. Thus we can include frustration in a continuous field theory by excluding the core of the line from the space and enclosing a source of the field ($\tilde{C}_\mu$) in the puncture, in the form of a line of quenched curvature.

The corresponding defect in the continuous random network model of glass may be the lines threading odd numbered rings (Rivier 1979) which again cannot end within the medium. Such odd rings are often present at the core of crystalline disclinations (rotation dislocations) and parallel transport around a disclination core results in a finite rotation of the lattice vectors (this is clearly illustrated in Lardner p.266) thus again the centre of the punctures are associated with lines of finite curvature.

All glasses must, in fact, have some additional constraints imposed on the equation 3.40 because the free energy density is, in general, spacially fluctuating and history dependent. We introduce these constraints by excluding regions of the space (punctures) and imposing boundary conditions on the surface of the punctures, which take the form of lines of quenched curvature within them. The curvature acts as a source of the distortion field ($\tilde{C}_\mu$) because, for any contour surrounding the holes

$$\mathrm{Tr}\ \mathrm{Ps}\ \exp \oint \tilde{G}_\mu\, dx^\mu = I \qquad 3.42$$

Here I is the invariant associated with a line defect in a nonabelian model. When the curvature $(\tilde{F}\mu\upsilon)$ is small

$$I = \mathrm{Tr}\ \exp \tilde{F}^{\mu\upsilon}\ dS\mu\upsilon \qquad 3.43$$

$dS\mu\upsilon$ represents the cross section area of the puncture in the $\mu\upsilon$ plane. Equation 3.42 implies that for a single straight defect (with axisymmetric symmetry) the magnitude of $\tilde{C}\mu$ must decrease as the inverse of the distance from the line. The free energy density, with a Lagrange multiplier included to quench the curvature in the hole, is

$$f(\underline{x}) = \gamma g^2\lambda_0{}^2[\tilde{C}_\mu(\underline{x}),\hat{\Omega}_0]^{ij}[\tilde{C}_\mu(\underline{x}),\hat{\Omega}_0]^{ij} + \tilde{F}\mu\upsilon^{ij}\tilde{F}\mu\upsilon^{ij}$$
$$+ \Lambda^{ij}_{\mu\upsilon}(\tilde{F}^{ij}_{\mu\upsilon}-\overset{Q}{\tilde{F}}{}^{ij}_{\mu\upsilon}) \qquad 3.44$$

with the corresponding Euler Lagrange equations

$$\varepsilon^{ijk}\{\tilde{D}\mu\tilde{F}^{ij}_{\mu\upsilon} - \gamma\lambda_0^2\ g^2[[\tilde{C}\nu,\hat{\Omega}_0],\hat{\Omega}_0{}^{-1}]^{ij} = \tilde{D}\mu\Lambda^{ij}_{\mu\upsilon}(\underline{x})\} \qquad 3.45$$

The general solution of these nonlinear differential equations is inaccessible, however it is possible to ennumerate the number of distinct ground state configurations. Suppose, for example, there is a unique solution of 3.45 which gives the minimum energy configuration of the field $\{\tilde{C}\mu(\underline{x})\}$. However there are many configurations of the matter field $\{\hat{A}\mu(\underline{x}),\hat{\Omega}(\underline{x})\}$ corresponding to $\{\tilde{C}\mu(\underline{x})\}$, all related to each other by gauge transformations.

$$\hat{\Omega}^{1}(\underline{x}) = \hat{U}(\underline{x}) \quad \hat{\Omega}(\underline{x}) \; \hat{U}^{-1}(\underline{x})$$

$$\hat{\Lambda}^{1} \; (\underline{x}) = \hat{U}(\underline{x})\hat{\Lambda}_{\mu}\hat{U}^{-1}(\underline{x}) - g^{-1} \; \hat{U}(\underline{x}) \, \partial_{\mu} \hat{U}^{-1} \, (\underline{x})$$

$$\tilde{C}^{1}_{\mu}(\underline{x}) = \tilde{C}_{\mu}(\underline{x})$$

In a simply connected medium all such gauge transformations are equivalent and the configurations all correspond to the same physical state. In the presence of punctures this is not the case as the holes introduce additional solutions which would be inadmissible in a continuous space.

The matter field configuration on a contour around a given puncture can be parameterized by $\hat{W}(\underline{x})$ which defines a map of S^{1} (a circle) onto SO(3) and such maps can be divided into equivalent classes, corresponding to the elements of the first homotopy group (Π_1 (SO(3)). As we saw in chapter 2, $\Pi_1(SO(3)) = Z_2$ and thus there are two distinct classes of maps, corresponding to a rotation of the matter field by 0 or 2π around the contour (labelled by $|0\rangle$ and $|2\pi\rangle$ respectively). The $|2\pi\rangle$ states would have been inadmissible as a ground state configuration in a continuous space as they include a singularity of the matter field which, in our case, is contained within the puncture and does not cost any energy. The gauge transformations ($\hat{U}(\underline{x}) \in SO(3)$) on this contour also fall into two distinct classes, for the same reason, and any gauge transformation belonging to the nontrivial element of the homotopy group has the effect of changing $|0\rangle$ into $|2\pi\rangle$ and vice versa (Jackiw 1980, Isham 1981). The intermediate configurations of the matter field in a large (nontrivial) gauge transformation have a singular plane, bounded by the puncture under consideration (as in figure 2.2). Thus the transition from the state $|0\rangle$ to $|2\pi\rangle$ (or $|2\pi\rangle$ to $|0\rangle$) of any defect involves tunnelling through an energy barrier caused by the singular plane in the intermediate state, and the size of the barrier is related to the minimum area spanned by the puncture (size of the intrinsic defect). The initial and final configurations have the same energy because the $\tilde{C}\mu$ field is unchanged.

Thus associated with every puncture (line defect) of the medium are two distinct equal energy configurations, separated by an energy barrier. The Hamiltonian of one such two level system (energy E) can be written as

$$H = \begin{pmatrix} E & \Delta_o \\ \Delta_o & E \end{pmatrix} \begin{pmatrix} |0\rangle \\ |2\pi\rangle \end{pmatrix} \qquad 3.46$$

where Δ_o represents the tunnelling matrix element and is a measure of overlap between the states and it is a function of the energy barrier (hence the size of the defect). This equation has eigen values ($E \pm \Delta_0$) and eigen vectors ($|0> \pm |2\Pi>$) and thus the true ground states are the gauge invariant linear combinations of the states $|0>$ and $|2\Pi>$ with an energy splitting ($2\Delta_0$) which depends on the height of the barrier alone. The two level systems contribute to the specific heat (as discussed in chapter 1) in the following way:

$$C = \int_0^{\infty} \frac{\Delta_0^2}{(k T)^2} \text{Sech} \left(\frac{\Delta_0}{kT}\right) n(\Delta_0)\, d\Delta_0$$

$$= k^2 T \int_0^{\infty} dx\, x^2\, \text{Sech}^2 x \;\; n(xkT)$$

$$\left(x = \frac{\Delta_0}{kT}\right)$$

$$= \frac{\Pi^2}{12} r(o)\, k^2 T$$

as long as $n(\Delta_0)$ (the density of states with splitting Δ_0) is independent of Δ_0 for $\Delta_0 \lesssim k_\beta T$. Hence the two configurations per defect will have a linear contribution to the specific heat if there is a uniform distribution of overlap integrals (Δ_0) in the system, over an energy scale corresponding to a few degrees Kelvin. This differs from the usual assumption of a uniform distribution of energy splitting (Δ in fig. 1.2) because here Δ is always zero. Experimentally one observes the distribution of the total splitting ($P((\Delta^2 + \Delta_0^2)^{\frac{1}{2}})$) and it is impossible to separate the contribution from the splitting distribution ($g(\Delta)$) and the overlap integral distribution ($n(\Delta o)$).

In summary, the coexistence of gauge invariance and intrinsic defects (punctures) in glasses introduces a number of distinct ground state configurations (two per defect) and the system can tunnel between these configurations via large (nontrivial) gauge transformations. A uniform distribution of tunnelling amplitudes will lead to a specific heat contribution which has a linear temperature dependence and a thermal conductivity $k \alpha T^2$, effects which are observed in most glasses at low temperatures.

3.4 Excitations from the Ground State

In the above discussion we considered the low temperature properties of glasses and the intrinsic defects of the ground state. Such defects are frozen in to the system and cannot move or be eliminated by relaxation. In addition to the frozen defects there are topologically stable excitations from the ground state, or line defects, which can move freely within the medium. Such excitations can be classified by the homotopy groups of the mapping

$$\hat{W}(\underline{x}) : \Sigma \rightarrow SO(3)$$

and again line singularities, associated with a rotation of the matter field by 2Π on any contour surrounding the line, are the only stable defects. The energy of the defect depends on the gauge field which tends to screen the distortion induced by the singularity.

A similar situation arises in Type II superconductors which can be described by an abelian gauge theory. The wavefunctions (matter field) $|\Psi|e^{i\theta}$ must be single valued and the defects (vortices) are labelled by an integer (n) with $\oint \underline{\nabla\theta} . d\underline{\ell} = 2\Pi n$. The Euler Lagrange equations for the Abelian model can be solved explicitly, at least for a single vortex (Tinkham 1975) and it is found that the magnetic induction (curvature) decays as the logarithm of the distance from the defect (r) for small r and expodentially for large r (greater than the penetration depth). One possible solution of the equations is $\underline{A} = g^{-1} \underline{\nabla\theta}$ (or $\underline{C} = g^{-1} \underline{\nabla}\theta - \underline{A} = 0$) everywhere, except on the core of the vortex, however such a defect would have an enormous core energy. The total energy is reduced by spreading the curvature ($\underline{\nabla} \times \underline{A}$) over a large region of space (of the order of the penetration depth) and outside this region the distortion ($\underline{C}$) is approximately zero. The matter field singularity cannot spread in this way because of the single valued nature of this field.

The nonlinear equations of the nonabelian model makes an explicit solution of the Euler Lagrange equations (3.45) inaccessible, however we expect a similar effect to occur. Topological excitations are associated with a matter field singularity, but the distortion ($\tilde{C}_\mu$ field) is screened by the gauge field which has a finite curvature ($\tilde{F}_{\mu\upsilon}$) in a region of space, the size of which is determined by the length scale of the inhomogeneity of the $\tilde{C}_\mu$ field.

The length scale (ℓ) can be estimated from the Euler Lagrange equations (3.45), by writing them in terms of dimensionless variables:

$$\tilde{C}^{\upsilon 1} = \ell g \tilde{C}^{\upsilon} \qquad 3.47$$

$$\partial^1_\mu = \ell \frac{\partial}{\partial x_\mu} = \ell \partial_\mu \qquad 3.48$$

Then $\tilde{F}^{\mu\upsilon 1} = \partial^{1\mu} C^{1\upsilon} - \partial^{1\upsilon}\tilde{C}^{1\mu} + [\tilde{C}^{1\mu}, \tilde{C}^{1\upsilon}] \qquad 3.49$

$$= g\ell^2 \tilde{F}^{\mu\upsilon} \qquad 3.50$$

Equation 3.45 becomes

$$\varepsilon^{ijk} \{ \frac{1}{\ell^3 g} [\tilde{D}^1_\mu \tilde{F}^{\mu\upsilon}]^{ij} - \frac{\gamma\lambda_0{}^2 g^2}{\ell g} [[\tilde{C}^1_\nu, \hat{\Omega}_0], \hat{\Omega}_0^{-1}] \} = 0 \qquad 3.51$$

or $$\varepsilon^{ijk} \{ \frac{1}{\ell^2 \gamma\lambda_0{}^2 g^2} [D^1_\mu \tilde{F}^1_{\mu\upsilon}]^{ij} - [[\tilde{C}^1_\nu, \hat{\Omega}_0], \hat{\Omega}_0^{-1}]^{ij} \} = 0 \qquad 3.52$$

and the length scale associated with the inhomogeneities of the $\tilde{C}_\mu$ field is $\ell = (\gamma^{\frac{1}{2}}\lambda_0 g)^{-1}$. This is analogous to the penetration depth in a superconductor and it is a measure of the size of the region in which the curvature ($\tilde{F}_{\mu\upsilon}$) and $\tilde{C}_\mu$ are finite, for a single defect.

When there is a large number of defects in the system, which tend to screen each others distortion field, the spacial fluctuations (and thus the derivatives) scale with a different length ℓ^1 equal to the average distance between the defects therefore we define $\partial''_\mu = \ell^1 \partial_\mu$. For a relatively high defect concentration (high enough for defect loops to interact with each other) $\ell^1 = \rho^{-\frac{1}{2}}$ where ρ is the total length of defect per unit volume.

Now $$\tilde{F}^{\mu\upsilon} = \frac{1}{g\ell}\left(\frac{1}{\ell^1}\left(\partial''^{\mu}\tilde{C}^{1\upsilon} - \partial''^{\upsilon}\tilde{C}^{1\mu}\right) + \frac{1}{\ell}\left[\tilde{C}^{1\mu},\tilde{C}^{1\upsilon}\right]\right) \qquad 3.53$$

and $$f(\underline{x}) = \frac{1}{g\ell^2}\left[\frac{1}{\ell^1}\left(\partial''^{\mu}\tilde{C}^{1\upsilon} - \partial''^{\upsilon}\tilde{C}^{1\mu}\right) + \frac{1}{\ell}\left[\tilde{C}^{1\mu},\tilde{C}^{1\upsilon}\right]\right]^{ij} \times$$

$$\left[\frac{1}{\ell^1}\left(\partial''^{\mu}\tilde{C}^{1\upsilon} - \partial''^{\upsilon}\tilde{C}^{1\mu}\right) + \frac{1}{\ell}\left[\tilde{C}^{1\mu},\tilde{C}^{1\upsilon}\right]\right]^{ij} + \frac{1}{g^2\ell^4}\left[\tilde{C}^1_\mu, \hat{\Omega}_o\right]^{ij}$$

$$\left[\tilde{C}^1_\mu, \hat{\Omega}_o\right]^{ij} \qquad 3.54$$

Thus in the regime where $\rho^{-\frac{1}{2}} = \ell^1 \ll \ell$ (the semi dilute regime) the derivative terms dominate the free energy.

ie $$f(\underline{x}) = \frac{1}{g^2\ell^2\ell'^2} = \left(\partial''^{\mu}\tilde{C}^{1\upsilon} - \partial''^{\upsilon}\tilde{C}^{1\mu}\right)^{ij}\left(\partial''^{\mu}\tilde{C}^{1\upsilon} - \partial''^{\upsilon}\tilde{C}^{\mu}\right)^{ij} \qquad 3.55$$

with the Euler Lagrange Equation

$$\partial_\mu\partial^\mu \tilde{C}^{1\upsilon}(\underline{x}) - \partial_\mu\partial^\upsilon\tilde{C}^{1\mu}(\underline{x}) = \tilde{J}^\upsilon(\underline{x}) \quad \delta^2(\underline{x} - \underline{\ell}) \qquad 3.56$$

The two dimensional δ function is included because the Euler Lagrange Equation is not satisfied on the defect cores. This equation can be solved by fixing the gauge such that

$$\partial_\upsilon \tilde{C}^\upsilon = 0 \qquad 3.57$$

which is consistent with equation 3.17 in the semi dilute regime. In terms of the $\tilde{C}$ field 3.17 becomes

$$\tilde{D}_\mu [\tilde{C}^\upsilon, \hat{\Omega}_0] = 0 \qquad 3.58$$

$$[\tilde{D}_\mu \tilde{C}^\upsilon, \hat{\Omega}_0] + [\tilde{C}^\mu, [\tilde{C}^\upsilon, \Omega_0]] = 0 \qquad 3.59$$

Thus when the gradient terms dominate equation 3.57 is a solution of 3.59. Now 3.56 becomes

$$\partial_\mu \partial^\upsilon \tilde{C}^\mu (\underline{x}) = \tilde{J}^\upsilon(\underline{x}) \quad \delta^2 (\underline{x} - \ell) \qquad 3.60$$

and imposing the boundary condition $\tilde{C}^\mu = 0$ at infinity we have

$$\tilde{C}^\upsilon = - \int d^3\underline{x}' \quad \tilde{J}^\upsilon \frac{(x') \; \delta^2 \; (x'-\ell)}{1\underline{x}-\underline{x}'1} \qquad 3.61$$

The free energy, after integrating by parts, becomes

$$F = \int d^3\underline{x} \; \mathrm{Tr} \; (-\tilde{C}_\mu \partial_\nu \partial^\upsilon \tilde{C}^\mu + \tilde{C}_\mu \partial_\mu \partial^\mu \tilde{C}^\upsilon) \qquad 3.62$$

$$= \int d^3\underline{x}' \int d^3\underline{x} \frac{(\tilde{J}^\upsilon(x) \; \tilde{J}^\upsilon(x'))}{|x - \underline{x}'|} \quad \delta^2(\underline{x} - \ell) \; \delta^2(\underline{x}' - \ell^1)$$

$$= \sum_{ij} \int d\ell_i \int d\ell_j \quad \mathrm{Tr} \frac{[\tilde{J}^\upsilon (\ell_i) \; \tilde{J}^\upsilon(\ell_j)]}{|\underline{x}_i - \underline{x}_j|} \qquad 3.63$$

where i, j label the line defects.

Thus, in the semi dilute regime, the interaction energy of vortices has the usual form for line defects, as discussed in chapter 2. Such defects could indeed be the excitations which dominate the relaxation processes of supercooled liquids and lead to the observed Vogel Fulcher law.

3.5 Conclusions

In this chapter we constructed a field theory of glass in which the macroscopic homogeneity was formulated as a local invariance of the free energy. The intrinsic defects are included as punctures containing lines of quenched curvature and these act as sources of distortion in the medium. A quenched, entangled mass of defect lines exist in the ground state of all glasses. Associated with each such line are two distinct solutions of the Euler Lagrange equations (minimum energy configurations) related to each other by a large (nontrivial) gauge transformation. The gauge invariant linear combination of these states constitutes a doublet with an energy splitting which depends on the size of the defect loop. This is, in fact, a universal model for the two level system of glasses which is a direct consequence of the co-existence of gauge invariance and line defects in these materials.

In addition to the ground states, there are other, (metastable) solutions of the Euler Lagrange equations, corresponding to topologically stable excitations of the matter field. These are analogous to vortices in an abelian model of a type II superconductor. The vortices are free to move and they interact via the usual $\frac{1}{r}$ potential, at least in the semi dilute regime. The matter field in the vicinity of the core of such a defect is significantly distorted and structural relaxation is possible in this region. Thus vortices have all the properties of the line defects discussed in the previous section, hence they could be responsible for the Vogel Fulcher law of the relaxation properties of supercooled liquids.

CHAPTER 4

A CONTINUOUS FIELD THEORY OF SPIN.GLASS

4.1 Introduction

In the previous chapter we introduced a phenomenological field theory of glasses, in which the gauge invariance played a significant role. It should, in principle, be possible to derive the continuum free energy from the Edwards Anderson model of spin glass, or from the Keating model for covalent materials, both models being inherently discrete. In this chapter we develop a continuum version of the Edwards Anderson model but it does not bear much resemblance to the previous treatment. The main reason for the discrepancy is that here the gauge fields are derived from the (quenched) interactions and as such they are not independent dynamical variables. This eliminates the possibility of tunnelling between ground states by means of a gauge transformation, however the frustration lines remain as lines of finite curvature and these lines are associated with low energy excitations which have all the properties of the two level system introduced by Anderson, Halperin, Varma and Phillips.

4.2 The Discrete Model

As a starting point for our field theory we consider the Edwards Anderson Hamiltonian for a spin glass

(Edwards and Anderson 1975) in which the spins ($\underline{S}i$) reside on a lattice with random nearest neighbour interactions (Jij). The interactions can be random in sign and magnitude, or in sign alone.

$$H = - \sum_{<ij>} J_{ij} \, \underline{S}_i \cdot \underline{S}_j \qquad 4.1$$

Here i, j label the sites of the lattice and the sum is over all nearest neighbour pairs of sites (bonds). The model displays a discrete gauge invariance (Toulouse 1977) as the local transformation:

$$\underline{S}_i \to - \underline{S}i$$

$$J_{ij} \to - J_{ij} \text{ for all j nearest neighbours to i}$$

leaves the Hamiltonian unchanged.

In fact the interactions are generally quenched a priori and the system is not free to take advantage of the gauge invariance. However the partition function is also gauge invariant (Fradkin et al 1978) as for a particular configuration {J}:

$$Z \{J\} = \sum_{\{si\}} \exp -\beta \sum_{<ij>} J_{ij} \, \underline{S}i \cdot \underline{S}j \qquad 4.2$$

For a second configuration $\{J^1\}$, related to the first by

$$J^1_{ij} = \zeta_i \, J_{ij} \, \zeta_j \qquad (\zeta_i, \zeta_j = \pm 1)$$

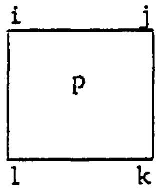
$$Z \{J^1\} = \sum_{\{si\}} \exp -\beta \sum_{<ij>} J_{ij} \, \zeta_i \, \underline{S}i \cdot \zeta_j \, \underline{S}j$$

$$= \sum_{\{si\}} \exp -\beta \sum_{<ij>} J_{ij} \, \underline{S}^1_i \cdot \underline{S}^1_j$$

$$= Z \{J\} \qquad 4.3$$

The partition function is the same for all configurations of J related to each other by a gauge transformation. All such configurations have the same frustration function $\{\Phi p\}$ which is defined for any plaquette p and by the product of the interactions of the bonds on the plaquette.

$$\Phi p = J_{ij} \, J_{jk} \, J_{kl} \, J_{li} \qquad 4.4$$



Φp is gauge invariant and as such it is possible to sum over all configurations of J which leave this combination unchanged:

$$\sum_{\{J\}}{}^{1} Z \; \{J\} = 2^N \; Z \; \{\Phi\} \qquad 4.5$$

and
$$Z\{\Phi\} = 2-N \sum_{\{J\}} \prod_p (\delta(J_{ij}J_{jk}J_{kl}J_{li}\Phi_p - 1)$$
$$\sum_{\{S\}} \exp -\beta \sum_{<ij>} \underline{S}_i \, J_{ij} \, \underline{S}_j \qquad 4.6$$

The restricted sum is over all configurations of J related by a gauge transformation. Thus, as far as the statistical mechanics are concerned, it is possible to consider the interactions as dynamical variables which must obey certain constraints.

Equation 4.1 can be generalized to

$$H = - \sum_{ij} \underline{S}i^T \; \underline{\underline{J}}_{ij} \; \underline{S}j \qquad 4.6$$

where $\hat{J}_{ij} = \frac{\underline{\underline{J}}_{ij}}{J} \in SO(3)$ is a rotation matrix .

Equations 4.1 and 4.6 are equivalent when the rotations are restricted to angles of 0 and Π and there is no physical justification for including any other angles. The generalized model is, however, invariant under the continuous gauge transformation:-

$$\underline{S}_j \rightarrow \underline{\underline{O}}_j \; S_j \qquad \underline{\underline{O}}_j \; \in SO(3)$$

$$\underline{S}_i^T \rightarrow \underline{S}_i^T \; \underline{O}_i^T$$

and $\underline{\underline{J}}_{ij} \rightarrow \underline{\underline{O}}_i \; \underline{\underline{J}}_{ij} \; \underline{\underline{O}}_j^T$

Lattice gauge theories of this type have been extensively studied by particle physicists (Wilson 1974). Here $\underline{\underline{J}}$ plays the role of the gauge field and, when all rotations are small, the discrete Hamiltonian has a limit for infinitesimal lattice spacings which is the usual minimally coupled continuum Hamiltonian (Balian et al 1974).

For a spin glass this continuum limit is inappropriate as the rotations cannot, by any stretch of the imagination, be considered to be infinitesimal. Not only are the gauge rotations finite but the rotation of one spin with respect to its neighbour may also be large, hence the field gradient cannot be defined. However the combination of the two rotations is, in general, small and this variable may be a good candidate for the field in a continuum model of spin glass. We therefore define a rotation matrix ($\underline{\underline{R}}_{ij}$) on the bond connecting the two spins (in a particular orientation) at sites i and j as follows:-

$$\underline{S}_j = \underline{\underline{R}}_{ji}\,\underline{S}_i \qquad 4.7$$

and $$\underline{S}_i = \underline{\underline{R}}_{ij}\,\underline{S}_j \qquad 4.8$$

The orientation of the bond is important and this is reflected in the ordering of the site labels:-

$$\underline{\underline{R}}_{ij} = \underline{\underline{R}}^{-1}_{ji} \qquad 4.9$$

The ambiguity in this definition of $\underline{\underline{R}}_{ij}$ is eliminated by choosing the rotation axis to be perpendicular to the plane formed by the direction of the two spins. $\hat{Z}_{ij} = (\underline{S}_i \times \underline{S}_j)/|\underline{S}_i \times \underline{S}_j|$. In a similar way $\hat{J}_{ij}$ is a rotation about $\hat{Z}_{ij}$ defined by:-

$$\underline{S}^1_j = \hat{J}_{ji}\,\underline{S}_i \qquad 4.10$$

$\underline{S}^1_j$ is the minimum energy configuration of the spin at site j, for a particular $\underline{S}_i$ and $\hat{Z}_{ij}$. Now $\hat{J}_{ij}$ is not quenched but the magnitude of the rotation is quenched (to 0 or Π) and the axis of rotation is fixed by the configuration of the spins at i and j (therefore by $\underline{\underline{R}}_{ij}$). We see then that although $\underline{\underline{R}}_{ij}$ and $\hat{J}_{ij}$ are dynamical variables they are not independent. The combination of the two rotations $\hat{J}_{ji}\,\underline{\underline{R}}_{ij}$ represents a small rotation of θ_{ij} about

about the axis $\hat{Z}ij$ (Fig. 4.1) and as such it can be expanded in terms of an infinitesimal antisymmetric matrix ($ga\ \underline{\underline{A}}ij$) belonging to the Lie Algebra of SO(3):-

$$\hat{J}ij\ \underline{\underline{R}}ji = \mathbb{1} + ga\ \underline{\underline{A}}ij + g^2a^2\underline{\underline{A}}^2ij + O(g^3) \tag{4.11}$$

Therefore the Hamiltonian (equation 4.6) can be written as:-

$$H = -\sum_{<ij>} \underline{S}_i^T\ \underline{\underline{J}}ij\ \underline{S}j$$

$$= -J \sum_{<ij>} \underline{S}_i^T\ \hat{J}ij\ \underline{\underline{R}}ji\ \underline{S}i \tag{4.12}$$

$$= -J \sum_{<ij>} \underline{S}_i^T\ (\mathbb{1} + ga\ \underline{\underline{A}}ij + g^2a^2\underline{\underline{A}}^2ij + O(g^3))\ \underline{\underline{S}}i \tag{4.13}$$

$$= -J \sum_{<ij>} S^2 + ga\ \underline{S}_i^T\ \underline{\underline{A}}ij\ \underline{\underline{S}}i + g^2a^2\underline{S}_i^T\ \underline{\underline{A}}^2ij\ \underline{S}i \tag{4.14}$$

The first term is an irrelevant constant and the second term vanishes therefore

$$H = g^2a^2J \sum_{ij} (\underline{\underline{A}}ij\ \underline{S}i)^T (\underline{\underline{A}}ij\ \underline{S}i) \tag{4.15}$$

$$= g^2a^2J \sum_{<ij>} |S|^2\ \theta^2ij \tag{4.16}$$

$$= g^2a^2J \sum_{<ij>} \mathrm{Tr}\ (\underline{\underline{A}}^2ij) \text{ (setting } |S| = 1) \tag{4.17}$$

The field ($\underline{\underline{A}}ij$) is gauge covariant:-

$$\underline{S}j \rightarrow \underline{\underline{O}}j\ \underline{S}j \qquad\qquad \underline{S}_i^T \rightarrow \underline{S}_i^T\ \underline{\underline{O}}_i^T$$

$$\hat{J}ij \rightarrow \underline{\underline{O}}i \;\; \hat{J}ij \; \underline{\underline{O}}_j^T \quad \text{and} \quad \underline{\underline{R}}ji \rightarrow \underline{\underline{O}}j \; \underline{\underline{R}}ji \; \underline{\underline{O}}_i^T$$

therefore $\hat{J}ij \; \underline{\underline{R}}ji \rightarrow \underline{\underline{O}}i \; \hat{J}ij \; \underline{\underline{R}}ji \; \underline{\underline{O}}_i^T$

and $\underline{\underline{A}}ij \rightarrow \underline{\underline{O}}i \; \underline{\underline{A}}ij \; \underline{\underline{O}}_i^T$

They are not, however, independent variables as they must obey a number of constraints (one for every independent cycle of the lattice) imposed by the nature of the lattice (the interactions) on which the spins reside. We have now replaced the site variables (the spins) with bond variables ($\underline{\underline{A}}ij$) on which constraints must be imposed.

4.3 Defects and Constraints

The intrinsic defects of a spin glass are frustration lines, the lines threading the plaquettes with an odd number of negative bonds. On such a plaquette it is impossible to find an orientation of the spins which minimizes the energy across all bonds simultaneously. Alternatively parallel transport of a spin around the plaquette does not return the spin to the initial configuration (Fig. 4.2) where parallel transport of a spin ($\underline{S}i$) from site i to site j is defined by $\hat{J}ji \; \underline{S}i$. Thus, on a frustrated plaquette P the ordered product of the interactions on the bonds ($\alpha\varepsilon p$) is not equal to the identity:-

$$\prod_{\alpha\varepsilon p} (\hat{J}\alpha) \; \underline{S}i \neq \underline{S}i$$

therefore $\prod\limits_{\alpha\varepsilon p} (\hat{J}\alpha) \neq \mathbb{1}$

In lattice gauge theory the plaquette variable

$$\mathfrak{C}p = \mathbb{1} - \prod_{\alpha\epsilon p} \hat{J}\alpha \tag{4.18}$$

is the discrete analog of the curvature $(F\mu\upsilon)$ in continuum models, and indeed they are equivalent in the limit of small rotations (Balian et al 1974). Thus frustration lines are lines of finite curvature in the discrete spin glass model.

For any particular configuration the spin field is single valued and the actual transport of a spin around any plaquette (defined by the ordered product of $\underline{R}\alpha$ around P) must return it to the initial configuration:-

$$\Big(\prod_{\alpha\epsilon p} \underline{\underline{R}}\alpha\Big)\,\underline{S} = \underline{S} \tag{4.19}$$

$$\text{However } \hat{J}\alpha\underline{\underline{R}}^{-1}_{\alpha} = e^{ga\,\underline{\underline{A}}\alpha} = \mathbb{1} + ga\,\underline{\underline{A}}\alpha + O(g^2)$$

$$\text{therefore } \underline{\underline{R}}\alpha = e^{-ag\underline{\underline{A}}\alpha}\,\hat{J}\alpha = (\mathbb{1} - ga\,\underline{\underline{A}}\alpha)\,\hat{J}\alpha + O(g^2) \tag{4.20}$$

and 4.19 will be satisfied for any spin if

$$\prod_{\alpha}\big(e^{-ga\underline{\underline{A}}\alpha}\,\hat{J}\alpha\big) = \prod_{\alpha}\big(\mathbb{1} - ga\,\underline{\underline{A}}_{\alpha} + O(g^2)\big)\,\hat{J}\alpha = \mathbb{1} \tag{4.21}$$

$$\text{or } \prod_{\alpha ep}\Big[\Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)\,e^{-ga\underline{\underline{A}}\alpha}\Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)^{-1}\Big]\prod_{\alpha ep}\hat{J}_\beta$$

$$= \Big(\mathbb{1} - ga\sum_{\alpha ep}\Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)\,\underline{\underline{A}}\alpha\,\Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)^{-1}\prod_{\alpha ep}\hat{J}_\alpha = \mathbb{1} \tag{4.22}$$

$$\text{Defining } e^{ga\tilde{A}\alpha} = \Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)\,e^{ga\underline{\underline{A}}\alpha}\,\Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)^{-1} \tag{4.23}$$

$$\text{or } \tilde{A}\alpha = \Big(\prod_{\beta<\alpha}\hat{J}_\beta\Big)\,\underline{\underline{A}}\alpha\,\Big(\prod_{\beta<\alpha}J_\beta\Big)^{-1} \tag{4.24}$$

$$\text{then } \mathbb{1} - \prod_{\alpha ep} e^{ga\tilde{A}\alpha} = \mathbb{1} - \prod_{\alpha ep}\hat{J}_\alpha = \mathfrak{C}p \tag{4.25}$$

All products in the above equations refer to path ordered products because the matrices do not, in general, commute. The left hand side of equation 4.25 is the usual definition of the curvature of the field $\tilde{A}$ thus we find that the lattice curvature $(\mathcal{G}p)$ must equal the curvature of $\tilde{A}$ and this acts as a constraint which must be included in the statistical mechanics of the model.

The above equations apply to the general nonabelian case, appropriate for Heisenberg spins. For x-y spins the group of transformations is SO(2) and all rotations commute, therefore

$$\underline{\underline{A}}_\alpha = \tilde{A}\alpha \quad \text{and} \quad \Big(\prod_{\alpha \epsilon p} e^{-ga\underline{\underline{A}}\alpha} \Big)\Big(\prod_{\alpha \epsilon p} \hat{J}\alpha \Big) = \mathbb{1} \qquad 4.26$$

$$\text{or} \quad \mathbb{1} - e^{ga\sum_{\alpha \epsilon p}\underline{\underline{A}}\alpha} = -ga \sum_{\alpha \epsilon p} \underline{\underline{A}}\alpha = \mathbb{1} - \prod_{\alpha \epsilon p} \hat{J}\alpha \qquad 4.27$$

The lattice curvature is, in this case, equal to the curvature of the actual gauge field $(\underline{\underline{A}}\alpha)$. The physical interpretation of this result is that the rotation of a spin around any closed contour must be zero (or 2Π) and as such the lattice rotation must be cancelled (modulo 2Π) by the gauge rotation.

4.4 A Continuum Model

The continuum limit of equation 4.17 is obtained by replacing the pair of site labels (i,j) by the position vector $(\underline{x})$ of site i and the direction label μ labelling the spacial direction of the bond (ij). Here we have confined our attention to a simple cubic lattice.

$$H = Ja^2 g^2 \sum_{\text{sites } (\underline{x})} \sum_{\mu = 1,2,3} \mathrm{Tr}(\underline{\underline{A}}\mu(\underline{x}))^2 \qquad 4.28$$

Replacing the sum over sites by an integral this becomes:

$$H = + \frac{J}{a} g^2 \sum_{\mu} \int dV \; \mathrm{Tr}\,(\underline{\underline{A}}\mu(\underline{x}))^2 \qquad 4.29$$

$$= \frac{J}{a} g^2 \int dV \; A^{ab}{}_{\mu}(\underline{x}) \; A^{ab}{}_{\mu}(\underline{x}) \qquad 4.30$$

$A^{ab}{}_{\mu}$ is antisymmetric in the indices (a and b) therefore we introduce a dual vector defined by:

$$A^{c}{}_{\mu} = \tfrac{1}{2} \varepsilon^{abc} \; A^{ab}{}_{\mu}$$

Thus $\underline{A}\mu$ is a vector in "isospin" space and

$$H = \frac{J}{a} e^2 \int dV \; \underline{A}\mu(\underline{x}) \; \underline{A}\mu(\underline{x}) \qquad 4.31$$

Now the three isospin vectors $(\underline{A}\mu(\underline{x}))$ are dynamical variables which must satisfy the constraints imposed by the lattice (equation 4.25) which, in the continuum model becomes

$$\mathbb{1} - P_{\ell} \, e^{g\oint \tilde{A}\mu d\ell_{\mu}} = \mathfrak{C} \qquad 4.32$$

Here P_{ℓ} is the path ordering operator and $\mathfrak{C}$ is the total lattice curvature within the contour.

4.5 The x-y Model

We now confine our attention to the Abelian x-y model which introduces a number of simplifications. In particular the isospin space is restricted to one dimension as the vector $\underline{A}\mu$ are all parallel (to the $\hat{Z}$ axis) and they can be parameterized by magnitude (Aμ) alone.

$$H = \frac{J}{a} g^2 \int dV \quad A_{\mu}^{(\underline{x})} A_{\mu}^{(\underline{x})} \qquad . \qquad 4.33$$

The curvature is also parallel to the axis and is related to the gauge field on an elementary surface in the μυ plane by:

$$F\mu\upsilon = \partial\mu A\upsilon - \partial\upsilon A\mu \qquad 4.34$$

In a ferromagnet (or Mattis model) the curvature is zero everywhere, except on the cores of vortices (excitations), where it has a magnitude of $2\Pi n$ (integer n). In a spin glass it is also finite on frustration lines where it has a magnitude $\pm\Pi$. Thus the constraints are imposed by quenching the curvature (at least to within a vortex excitation) everywhere in such a way that it is only finite on the frustration lines.

The partition function can be written as a functional integral over all configurations of $A\,\mu(\underline{x})$ which satisfy the constraints on the curvature:

$$Z = \int DA\mu(x)\ e^{-\beta\int d\underline{x} H(A\mu(\underline{x}))}\ \delta^{Q}_{(F_{\mu\upsilon}(\underline{x}) - (\partial\mu A\upsilon(\underline{x}) - \partial\nu A\mu(\underline{x})))} \qquad 4.33$$

This is, in some respects, the continuum analog of equation 4.6 for the discrete model. Introducing the dual vector $F_\eta^{Q} = \frac{1}{2}\epsilon_{\mu\upsilon\eta} \; F_{\mu\upsilon}^{Q}$ and writing the δ function in terms of a functional integral over an auxiliary field ($\underline{\Lambda}(\underline{x})$) this becomes

$$Z = \int D\Lambda_\eta(\underline{x}) \int DA\mu(\underline{x}) \ \exp - \int d\underline{x} \ [\frac{\beta J g^2}{a} \ A\mu(\underline{x}) \ A\mu(\underline{x})$$

$$+ i\Lambda\eta(\underline{x})(F\eta^Q(\underline{x}) - \mathcal{E}_{\eta\mu\upsilon}\partial\mu A\upsilon(\underline{x})] \qquad 4.34$$

Integrating by parts we have

$$Z = \int D\Lambda_\eta(\underline{x}) \int DA\mu(\underline{x}) \ \exp - \int d\underline{x} \ [\frac{\beta J g^2}{a} \ A\mu(\underline{x}) A\mu(\underline{x}) +$$

$$i\epsilon_{\eta\mu\upsilon}\partial\mu\Lambda\eta \ A_\upsilon(\underline{x}) + i\Lambda\eta(\underline{x}) \ F\eta^Q(\underline{x})] \qquad 4.35$$

The functional integral over the Λ field can be carried out by completing the square (Edwards 1958).

$$\int DC_i(\underline{x}) \ \exp - \tfrac{1}{2}\int d\underline{x} \int d\underline{y} \ C_i(\underline{x}) \ M_{ij} \ (\underline{x},\underline{y}) \ C_j(\underline{y}) - i\int d\underline{x}$$

$$X_i(\underline{x}) \quad C_i(\underline{x})$$

$$= N \ \exp -\tfrac{1}{2} \int d\underline{x} \int d\underline{y} \ X_i(\underline{x}) \quad M^{-1}_{ij}(\underline{x},\underline{y}) \ X_j(\underline{x}) \qquad 4.36$$

with $N = \int DC_i(\underline{x}) \ \exp -\tfrac{1}{2} \int d\underline{x} \int d\underline{y} \ C_i \ M^{-1}_{ij} \ (\underline{x},\underline{y}) C_j$ 4.37

Here $C\mu(\underline{x}) \ = A\mu(\underline{x})$

$M_{ij}(\underline{x},\underline{y}) = \delta_{ij}\delta(\underline{x}-\underline{y}) \ \ \frac{2\beta J g^2}{a}$

$X\upsilon \ = \ \mathcal{E}_{\eta\mu\upsilon} \ \partial\mu\Lambda_\eta$

therefore $Z = N_A \int D\Lambda_\upsilon(\underline{x}) \ \exp - \int d\underline{x}[\tfrac{1}{2}(\frac{2\beta J g^2}{a})^{-1}$

$$\varepsilon_{\eta\mu\upsilon}\partial\mu\Lambda\eta \ \varepsilon_{\delta\alpha\upsilon}\partial\alpha\Lambda\delta + i\Lambda_\eta(\underline{x}) F^Q_\eta(\underline{x})] \qquad 4.38$$

$$N_A = \int DA\mu(\underline{x}) \ \exp - \frac{\beta J g^2}{a} \ \int d\underline{x} \ A\mu(\underline{x}) \ A\mu(\underline{x}) \qquad 4.39$$

Rewriting equation 4.38 in q space

$$Z = N_A \int D\Lambda\upsilon(\underline{q}) \ \exp - (2\Pi)^3 \int d\underline{q}[+(\frac{4\beta J g^2}{a})^{-1}$$

$$\varepsilon_{\eta\mu\upsilon}\varepsilon_{\delta\alpha\upsilon}q_\mu q_\alpha \Lambda_\eta \Lambda_\delta \ + \tfrac{i}{2}(\Lambda\eta(\underline{q})F^Q\eta(\underline{-q}) + \Lambda\eta(\underline{-q})$$

$$F^Q_\eta \ (\underline{q}))] \qquad 4.40$$

with $\Lambda(\underline{q}) = \frac{1}{(2\Pi)^3} \int e^{-i\underline{q}\underline{x}} \Lambda(\underline{x})\, d^3\underline{x}$ 4.41

However $\varepsilon_{\eta\mu\upsilon}\, \varepsilon_{\sigma\alpha\upsilon}\, q_\mu q_\alpha = -q_\eta q_\sigma + q^2\, \delta_{\eta\sigma}$

and we can set $q_\sigma \Lambda_\sigma = 0$ which is, in effect, a continuity equation for Λ ($\underline{\nabla}.\underline{\Lambda} = 0$ in real space). This reflects the continuity equation for the curvature ($\underline{\nabla}.\underline{F}^Q = \underline{\nabla}.(\underline{\nabla} \times \underline{A}) \equiv 0$) and the fact that frustrated plaquettes are threaded through by continuous lines. Now $Z = N_A \int D\Lambda_\upsilon(q) \exp - (2\Pi)^3 \int dq \left(\frac{4\beta Jg^2}{a}\right)^{-1} \Lambda_\eta(\underline{q})\, q^2 \delta_{\eta\sigma} \Lambda_\sigma$

$$(-\underline{q}) + i\tfrac{1}{2}(\Lambda_\eta(\underline{q}) F_\eta^Q(-\underline{q}) + \Lambda_\eta(-\underline{q}) F_\eta^Q(\underline{q})] \qquad 4.42$$

$$= N_A N_\Lambda \exp - (2\Pi)^3 \left(\frac{4\beta Jg^2}{a}\right) \tfrac{1}{4} \int d\underline{q} \cdot F_\eta^Q(\underline{q}) \frac{1}{q^2} F^Q(-\underline{q}) \qquad 4.43$$

$$= N_A N_\Lambda \exp - \frac{1}{(2\Pi)^3} \left(\frac{\beta Jg^2}{a}\right) \int d\underline{x} \int d\underline{x}'\, F_\eta^Q(\underline{x}) F^Q_\eta(\underline{x}') \int d\underline{q}\; \frac{e^{-i\underline{q}.(\underline{x}-\underline{x}')}}{q^2} \qquad 4.44$$

$$\int d\underline{q}\, \frac{e^{i\underline{q}\cdot\underline{y}}}{q^2} = 2\Pi \int_0^\infty dq\, q^2 \int_{-1}^{+1} a\, \frac{e^{iqy\lambda}}{q^2}, \lambda = \mathrm{Cos}\theta$$

$$= \frac{2\Pi}{iy} \int_0^\infty dq\, \frac{e^{iqy} - e^{-iqy}}{q}$$

$$= \frac{2\Pi}{iy} \int_{-\infty}^{\infty} \frac{dq}{q}\, e^{iqy}$$

$$= + \frac{2\Pi^2}{y}$$

and equation 4.44 becomes

$$Z = N_A N_\Lambda \exp - \frac{\beta Jg^2}{4\Pi a} \int d\underline{x} \int d\underline{x}' \, \frac{F_\eta^Q(\underline{x}) . F_\eta^Q(\underline{x}')}{|\underline{x}-\underline{x}'|} \qquad 4.45$$

with $N_\Lambda = \int D\underline{\Lambda}(q) \exp\frac{-a\Pi^3}{\beta J g^2} \int d\underline{q}\, \underline{\Lambda}(\underline{q}) q^2 \underline{\Lambda}(-\underline{q})$ 4.46

The free energy is $F = \frac{-1}{\beta} \ln Z$

$$= -\frac{1}{\beta}(\ln N_A + \ln N_\Lambda) + F\text{int} \qquad 4.47$$

with $F\text{int} = \frac{Jg^2}{4\Pi a} \int d\underline{x} \int d\underline{x}' \frac{F_\eta^Q(x)\, F_\eta^Q(x')}{|\underline{x}-\underline{x}'|}$ 4.48

representing the ("antiferromagnetic") interaction between frustration lines.

The curvature is confined to a "tube" of constant cross section area (a^2) enclosing the frustration line and the continuity equation $\partial\eta F_\eta Q = 0$ implies that $F_\eta Q\, \hat{n}\eta$ is a constant ($\frac{1}{a^2} F^Q$) along the line ($\hat{n}$ is the tangent vector of the line). Therefore we can write $F_\eta^Q = F^Q \hat{n}_\eta$ 4.49

and $\int d\underline{x}\, \underline{F}_\eta^Q(\underline{x}) = \int d\ell \int ds \frac{F^Q}{a^2} \hat{n}_\eta$

$$= \int F^Q d\ell_\eta$$

$\int ds$ represents the integral over the cross section of the tube and $\int d\ell$ represents the integral along the length. For a frustration line $F^Q = \pm\Pi$ and the sign of F^Q can be used to determine the orientation of the line, leading to an interaction energy between two frustration lines (A,B) of

$$F_{AB} = \frac{Jg^2}{4} \Pi \int\int \frac{d\underline{\ell}_A \cdot d\underline{\ell}_B}{|\underline{x}_A - \underline{x}_B|} \qquad 4.50$$

This is the continuum version of the energy of frustration lines calculated in a discrete model by Fradkin et al (1978) .

4.6 The Two Level System

The curvature of the spin glass is quenched only to within the excitation of a vortex associated with a curvature of $2\Pi n$ along a continuous line in the medium. The excitation of a vortex (2Π) on a frustration line (with $F^Q = -\Pi$) has the effect of changing F^Q to $+\Pi$, thus reversing the orientation of the line (Fig. 4.3). The two configuration ($\pm\Pi$) correspond to the two chiralities discussed by Villain (1977), thus changing the chirality of a frustration line is equivalent to exciting a full vortex on the line.

For a single, isolated frustration loop the self energy is given by equation 4.50 with A = B.

$$F_{self} = \frac{Jg^2\Pi}{4} \iint \frac{d\underline{\ell}.d\underline{\ell}^1}{|\underline{x}-\underline{x}^1|} \qquad 4.51$$

Thus the self energy is invariant under a reversal of the line: $d\underline{\ell} \to -d\underline{\ell}$ and $d\underline{\ell}^1 \to -d\underline{\ell}^1$

therefore $F'_{self} = F_{self}$

The interaction energy with other defects is not invariant, however when the defect is surrounded by an isotropic distribution of defects the total interaction energy will be unchanged. Any anisotropy in the defect distribution will introduce an energy difference between the two line orientations.

The energy barrier separating the configurations arises from the fact that the vortex is a topologically nontrivial excitation. The intermediate configuration has a singular plane, bounded by the defect loop. It is this singular plane that is primarily responsible for the energy barrier therefore the height of the barrier is related to the area of the plane, hence to the length and shape of the defect loop.

Thus the two orientations of a frustration line are a good example of a two level system of the type introduced by Anderson et al (1972) and Phillips (1972) to explain the linear specific heat and other low temperature anomalies of glasses. Here a uniform distribution of energy splitting corresponds to a uniform distribution of anisotropy around the frustration lines.

4.7 Frustration Lines in the Heisenberg Model

For Heisenberg spins it is necessary to consider spin transformations belonging to the nonabelian rotation group (SO(3)). In this case it is the curvature associated with the modified gauge fields

($\tilde{A}$) that is quenched by the lattice with

$$\tilde{A}\alpha = \left(\prod_{\beta<\alpha} J\beta\right) \underline{\underline{A}}\alpha \left(\prod_{\beta<\alpha} J\beta\right)^{-1} \qquad 4.52$$

where α, β label the ordered links on some oriented path. In the presence of frustration the definition $\tilde{A}$ is path dependent, therefore not unique. However the $\tilde{A}$ field can be defined consistently for a given configuration of frustration lines by choosing a particular (arbitrary) set of surfaces bounded by the frustration loops, and a particular reference point Po. The ordered product in equation 4.52 is now defined along a path from Po to α, avoiding all cut surfaces. All such paths are, in fact, equivalent. In a similar way the curvature of a frustration loop is defined by the ordered product of J along a closed path starting (and finishing) at Po, and crossing the surface associated with that loop once, in a given (arbitrary) direction.

The above procedure is, in fact, equivalent to performing a gauge transformation to a configuration in which J = $\mathbb{1}$ everywhere, except on surfaces spanning the frustration lines.

As we demonstrated in section 4.2 the statistical mechanics are gauge invariant therefore the static properties will be unchanged by this transformation.

Thus, as before we have gauge fields $(\tilde{A}_{\mu}^{k}(\underline{x}))$ as the dynamical variables of a continuum model and these must satisfy constraints imposed by the lattice curvature and the partition function is given by:-

$$Z = \int D\tilde{A}_{\mu}^{k}(\underline{x}) \left(\exp - \frac{\beta J g^{2}}{a} \int d^{3}\underline{x}\ \tilde{A}_{\mu}^{k}(\underline{x})\ \tilde{A}_{\mu}^{k}(\underline{x})\right) \delta(\tilde{F}_{\mu\upsilon}^{Qk} - \tilde{F}_{\mu\upsilon}^{k}) \tag{4.53}$$

The curvature of a nonabelian model is a non linear function of the gauge field:

$$\tilde{F}_{\mu\upsilon}^{k} = \partial\mu\tilde{A}_{\upsilon}^{k} - \partial\upsilon\tilde{A}_{\mu}^{k} + g\varepsilon^{ijk}\ \tilde{A}_{\mu}^{i}\ \tilde{A}_{\upsilon}^{j} \tag{4.54}$$

or $$\tilde{F}_{\eta}^{k} = \tfrac{1}{2}\ \varepsilon_{\mu\upsilon\eta}\ \tilde{F}_{\mu\upsilon}^{k} = \varepsilon_{\mu\upsilon\eta}\ \partial\mu\tilde{A}_{\upsilon}^{k} + \frac{g}{2}\varepsilon^{ijk}\ \varepsilon_{\mu\upsilon\eta}\tilde{A}_{\mu}^{i}\ \tilde{A}_{\upsilon}^{j} \tag{4.55}$$

therefore:

$$\begin{aligned} Z = \int D\Lambda_{\mu}^{k}\int D\tilde{A}_{\mu}^{k} \exp - \int d^{3}\underline{x}\ \Big[\tilde{A}_{\mu}^{k}(\underline{x})\tilde{A}_{\mu}^{k}(\underline{x})\ \frac{\beta J g^{2}}{a} - \frac{ig}{2} \\ \Lambda_{\eta}^{k}\ \varepsilon^{ijk}\ \varepsilon_{\mu\upsilon\eta}\ \tilde{A}_{\mu}^{i}(\underline{x})\ \tilde{A}_{\nu}^{j}(\underline{x}) - i\Lambda_{\eta}^{k}\ \varepsilon_{\mu\upsilon\eta}\ \partial\mu A_{\upsilon}^{k} \\ + i\Lambda_{\eta}^{k}\ \tilde{F}_{\eta}^{Qk}\Big] \end{aligned} \tag{4.56}$$

Integrating by parts:

$$\begin{aligned} Z = \int D\Lambda_{\mu}^{k} \int D\tilde{A}_{\mu}^{k} \exp - \int d^{3}\underline{x}\ \Big[\frac{\beta J g^{2}}{a}\ \tilde{A}_{\mu}^{k}(\underline{x})\ \tilde{A}_{\mu}^{k}(\underline{x}) - \frac{ig}{2}\ \Lambda_{\eta}^{k}\ \varepsilon^{ijk} \\ \varepsilon_{\mu\upsilon\eta}\ \tilde{A}_{\mu}^{i}(\underline{x})\ \tilde{A}_{\nu}^{j}(\underline{x}) + i\partial_{\mu}\Lambda_{\eta}^{k}\,\varepsilon_{\mu\upsilon\eta}\ A_{\upsilon}^{k} + i\Lambda_{\eta}^{k}\ \tilde{F}_{\eta}^{Qk}\Big] \end{aligned} \tag{4.57}$$

We can now, formally at least, carry out the integral over $\tilde{A}(x)$:

$$\begin{aligned} Z = N_{A}\int D\Lambda_{\mu}^{k} \exp -\frac{1}{2} \int d^{3}\underline{x}\ \Big[\varepsilon_{\mu\upsilon\eta}\ \partial\mu\Lambda_{\eta}^{k}\ M^{-1\,kl}_{\upsilon\delta}\ \varepsilon_{\alpha\delta\beta}\ \partial_{\alpha}\ \Lambda_{\beta}^{l} \\ + i\Lambda_{\eta}^{k}\ \tilde{F}_{\eta}^{Qk}\Big] \end{aligned} \tag{4.58}$$

where $$M_{\sigma\lambda}^{ij} = \frac{2\beta J g^{2}}{a}\ \delta_{ij}\ \delta_{\sigma\lambda} - \frac{ig}{2}\ \varepsilon^{ijk}\ \varepsilon_{\sigma\lambda\upsilon}\ \Lambda_{\upsilon}^{k} \tag{4.59}$$

$$= \Lambda\,(\delta^{ij}\,\delta_{\sigma\lambda} - i\epsilon^{ijk}\,\epsilon_{\sigma\lambda\nu}\,\lambda^{k}_{\nu}) \qquad 4.60$$

where $\Lambda = \frac{2\beta J g^2}{a}$ and $\lambda^{k}_{\nu} = \frac{g}{2}\,\frac{a}{\beta J g^2}\,\Lambda^{k}_{\nu}$ 4.61

$$= g^{1}\,\Lambda^{k}_{\nu}$$

The inverse of M can, by inspection, be seen to have the following form:

$$M^{-1\,j\ell}_{\lambda\mu} = \frac{1}{\Lambda}\,(\delta^{j\ell}_{\lambda\mu} + i\epsilon^{j\ell m}\,\epsilon_{\lambda\mu\eta}\,\lambda^{m}_{\eta} + i^{2}\,\epsilon^{mjk}\,\epsilon^{nk\ell}$$

$$\epsilon_{\eta\lambda\delta}\,\epsilon_{\upsilon\delta\mu}\,\lambda^{m}_{\eta}\,\lambda^{n}_{\upsilon} + O(\lambda^{3})] \qquad 4.62$$

$$= \frac{1}{\Lambda}\,(\delta^{j\ell}_{\lambda\mu} + \sum_{n=1}^{\infty}\{[i\,\tilde{\epsilon}^{a}\,\tilde{\epsilon}_{\upsilon}\,\lambda^{a}_{\nu}]^{n}\}^{j\ell}_{\lambda\mu}) \qquad 4.63$$

where we write $(\tilde{\epsilon}^{a}\,\tilde{\epsilon}^{b})^{j\ell}$ to represent $\epsilon^{ajk}\,\epsilon^{bk\ell}$ and similarly for higher order products.

It is apparent that, since it is no longer gaussian, the functional integral over Λ cannot, in this case, be carried out exactly. However, when the constant

$$g' = \frac{a}{2\beta J g} \quad \text{is small (ie when} \quad k_{B}T << \frac{2}{a}\,Jg\,)$$

there is a natural expansion in terms of this parameter

and $M^{-1} = M_{o}^{-1} + (\Delta M)^{-1}$ 4.64

a with $M_{o}^{-1} = \frac{1}{\Lambda}\,\delta^{j\ell}_{\lambda\mu}$ 4.65

and $(\Delta M)^{-1} = \frac{1}{\Lambda}\sum_{n=1}^{\infty}[ig\tilde{\epsilon}^{a}\,\tilde{\epsilon}_{\nu}\Lambda^{a}_{\upsilon}]^{n}$ 4.66

Now, in q space, the partition function becomes:

$$Z = N_A \int D\Lambda^k_\mu(\underline{q})\left[\exp -(2\Pi)^3 \int d^3\underline{q} \quad \left(\frac{1}{2A}\Lambda^k_\eta(\underline{q})\varepsilon_{\mu\upsilon\eta}\,\varepsilon_{\alpha\upsilon\beta}q_\mu q_\alpha \Lambda^k_\beta(-\underline{q})\right.\right.$$

$$\left.\left. + i\Lambda^k_\eta \tilde{F}^{Qk}_\eta\right)\right]\left[\exp -\int d^3\underline{q}\frac{1}{2A}\Lambda^k_\eta(\underline{q})\varepsilon_{\mu\upsilon\eta}\,\varepsilon_{\alpha\lambda\beta}q_\mu q_\alpha (\Delta M^{-1})^{kl}_{\eta\lambda}\Lambda^1_\beta(-\underline{q})\right] \quad 4.67$$

$$= N_A N_\Lambda\left[\exp -(2\Pi)^3\left(\frac{\beta J g^2}{a}\right)\int d\underline{q}\tilde{F}^{Qk}_\eta(\underline{q})\frac{1}{q^2}\,\tilde{F}^{Qk}_\eta(-\underline{q})\right][1+0(g^1)] \quad 4.68$$

$$= N_A N_\Lambda\left[\exp -\frac{\beta J g^2}{4\Pi a}\int d\underline{x}\int d\underline{x}^1 \quad \frac{\tilde{F}^{Qk}_\eta(\underline{x})\;\tilde{F}^{Qk}_\eta(\underline{x}^1)}{|\underline{x}-\underline{x}^1|}\right][1+0(g^1)] \quad 4.69$$

Thus, at low temperatures ($k_\beta T << \frac{2}{a}Jg$) the interaction energy between frustration lines in a Heisenberg model has a similar form to that of an x-y model.

The continuity equation for the curvature in a non-abelian model is the Bianchi Identity:

$$\varepsilon_{\lambda\mu\upsilon} \quad D_\lambda \; \tilde{F}^k_{\mu\upsilon} = 0 \qquad 4.70$$

$$\text{or} \quad D_\lambda \; \tilde{F}_\lambda{}^k = 0 \qquad 4.71$$

$$\partial_\lambda \; \tilde{F}^k_\lambda = -g\varepsilon^{ijk} \; A^i_\lambda \; \tilde{F}^j_\lambda \qquad 4.72$$

However the curvature (isospace vector) is carried along the frustration lines therefore we can decouple the isospace and real space vectors and write:

$$F^k_\lambda = F^k\hat{n}_\lambda \qquad 4.73$$

Equation 4.72 becomes:

$$\partial_\lambda \; F^k = -g\varepsilon^{ijk} \; A^i_\lambda \; F^j \qquad 4.74$$

and the direction of the curvature (the rotation axis) can vary gradually along the line. The self interaction energy is:

$$F_{self} = \frac{Jg^2}{4\Pi} \iint d\underline{\ell} . d\underline{\ell}^1 \; \frac{\underline{F}^Q(\underline{x}) . \underline{F}^Q(\underline{x}^1)}{|\underline{x}-\underline{x}^1|} \qquad 4.75$$

The self energy of a frustration line is invariant under the transformation $d\underline{\ell} \to -d\underline{\ell}$ or equivalently $\underline{F}(\underline{x}) \to -\underline{F}(\underline{x})$) everywhere on the line. When the total magnitude of the rotation is Π(as it is for frustration lines) such a transformation is carried out by the excitation of a full vortex (rotation magnitude 2Π) on the line. In a ferromagnet such a vortex is not a topologically stable excitation but the noncollinearity of the spins in a spin glass stabilizes vortices with 2Π rotations (see chapter 2 and the next section). Thus the situation in Heisenberg spin glass at low temperatures is directly analogous to that of x-y spin glass.

4.8 Topological Excitations

In the x-y model of a spin glass vortex excitations, associated with a $2\Pi n$ rotation of the spin from the minimum energy configuration, are topologically stable defects. The single valued nature of the spin field requiresthat $\oint A\mu d\ell\mu = 2\Pi n$ (for n integer) on any contour not surrounding a frustration line and $\oint A\mu d\ell\mu = 2\Pi\ (n+1)$ when the contour surrounds a frustration line. The line integral can be transformed by Stoke's Theorem to a surface integral:

$$\int dS_{\mu\upsilon}(\partial_\mu A_\upsilon - \partial_\upsilon A_\mu) = 2\Pi n$$

$$= \int F_{\mu\upsilon}\, dS_{\mu\upsilon}$$

and the core of the vortex is associated with a large curvature of total magnitude $2\Pi n$. A vortex interacts with other vortices, and with frustration lines, with an energy given by equation 4.50 and as such the distortion field of topological defects is screened not only by other such defects, but also by the intrinsic defects (frustration lines) of the medium.

In chapter 2 we discussed how the energy of a density of defects (ρ), interacting via a $\frac{1}{r}$ potential, has the form (equation 2.27)

$$E(\rho) = \frac{B}{a}\rho - \frac{A}{a}\rho \ln \rho a^2$$

This was valid when the screening length was determined by the average distance between defects. In the presence of frustration lines there are two possible regimes 1) $\rho >> \rho_F$ (ρ_F is the total length of frustration line per unit volume). In this regime the screening length is the average distance between vortices and equation 2.27 is valid. 2) $\rho << \rho_F$. Screening, here, will be dominated by the frustration lines and equation 2.27 becomes:

$$E(\rho) = \frac{B}{a}\rho - \frac{A}{a}\rho \ln \rho_F a^2$$

$= \frac{B^1}{a}\rho$ because ρ_F is a constant for a given material

Thus the density of vortices in a spin glass will follow a Vogel Fulcher Law only in a medium with a dilute concentration of frustration lines.

In the Heisenberg model the constraints corresponding to equations 4.74 and 4.75 are

$$P \; e^{g\oint \tilde{A}_\mu d\ell_\mu} = \mathbb{1} \qquad 4.76$$

for a contour not surrounding a frustration line and

$$P \; e^{g\oint \tilde{A}_\mu d\ell_\mu} = \mathbb{1} - \mathbb{C} \qquad 4.77$$

for a contour surrounding a frustration line. Here $\mathbb{C}$ represents a rotation of Π about any axis. These equations are satisfied by total rotations of $2\Pi n$ about any axis. In a ferromagnet such a vortex is not stable, however in spin glass the noncollinearity of the spins stabilizes the vortex with $n = 1$ (see chapter 2). At low temperatures such vortices interact via a $\frac{1}{r}$ potential (equation 4.73) but at low temperature the screening will always be dominated by frustration lines (as the density of vortices will be small) thus it is unlikely that the density of defects in a Heisenberg model will follow a Fulcher law, in any temperature regime.

4.9 Conclusions

In this chapter we discussed a continuous field theory of spin glass in which the field was derived from the (infinitesimal) combination of the lattice rotation (interactions) and the actual rotation across a bond. The underlying lattice of interactions imposes constraints on the field, in the form of lines of finite curvature (frustration lines). In the x-y model the orientation of a frustration line is arbitrary and the self energy is invariant under the reversal of the line direction, effected via the excitation of a vortex. Such excitations represent a specific model for the two level system introduced to explain the low temperature anomalies of glasses.

In addition to the intrinsic defects (frustration lines) there are topologically stable excitations (vortices) which (in the x-y model and at low temperatures in the Heisenberg model) interact with other vortices and with frustration lines, via a $\frac{1}{r}$ potential. Such vortices can move freely in the medium and they may be absorbed by frustration lines, with the effect that the orientation of the frustration line is reversed. The equilibrium density of vortices in the x-y model (in a system with a dilute concentration of frustration lines) follows a Vogel Fulcher law which might explain the observation of this law for the spin relaxation time in recent experiments on spin glass (Thoulence 1980).

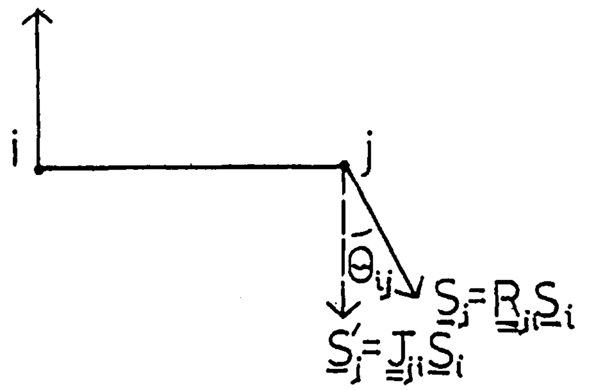


Figure 4.1

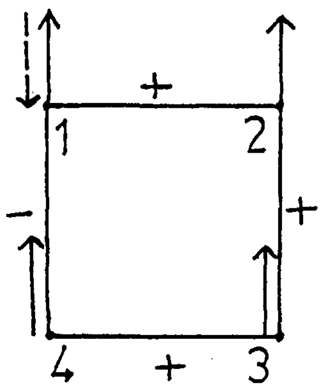


Figure 4.2

A Frustrated Plaquette:

Parallel transport around the plaquette has the effect of rotating the spin by Π.

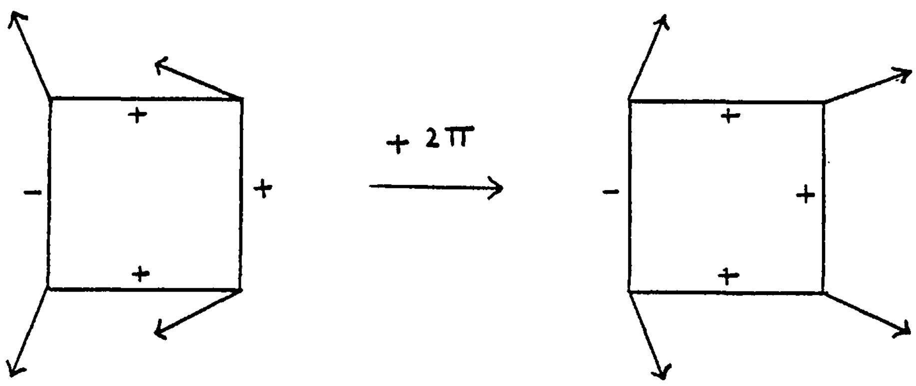


Figure 4.3

The two chiralities of a frustrated plaquette in the x-y model (after Villain 1977).

CHAPTER 5

DISCRETE MODEL OF COVALENT GLASS

5.1 Introduction

In this chapter we show that covalent glass can be approached in a similar way to spin glass by writing the random Keating model in a form which makes the gauge invariance evident. Again a field is derived from the combination of the actual rotation between two neighbouring bonds and the corresponding minimum energy rotation. However all rings of bonds must close therefore constraints (in the form of torsion and curvature) are imposed on the field and these act as extended sources of distortion in the network. Such constraints play the role of intrinsic defects in covalent glasses.

5.2 The Gauge Invariant Keating Model

The most successful model of covalent glass is the continuous random network (Polk 1971, Zachariasen 1932) in which every atom has a similar environment (co-ordination number, bond lengths and, approximately, the angles between the bonds) to that of the corresponding crystal, but the structure as a whole is random. The energy of this structure can be described by the Keating Model which was originally proposed for diamond (Keating 1966) but has since been used to study the vibrational properties of covalent glasses (Alben et al 1975).

$$U = \sum_{\ell=1}^{N_A}\left[\frac{\alpha}{2a^2}\sum_{\mu=1}^{Z}\left(\underline{x}_{\ell\mu}^2-a^2\right)^2 + \frac{\beta}{2a^2}\sum_{\mu,\upsilon>\mu}^{Z}\right.$$

$$\left.\left(\underline{x}_{\ell\mu}\cdot\underline{x}_{\ell\upsilon}-a^2\,\mathrm{Cos}^2\theta\right)^2\right] \qquad 5.1$$

Here $\underline{x}_{\ell\mu} = \underline{x}(\ell) - \underline{x}(\ell\mu)$ with $\underline{x}(\ell)$ representing the position of atom ℓ and $\underline{x}(\ell\mu)$ the position of the atom linked to ℓ by the bond μ. Z is the co-ordination number and a is the equilibrium bond length.

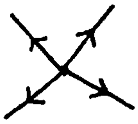
The first term is the bond stretching energy, with α the corresponding force constant and the second term is bond bending energy due to the deviation of the angle between bond pairs from the equilibrium value θ (for a tetrahedrally co-ordinated network $\mathrm{Cos}\theta = -\frac{1}{2}, \theta \sim 109^{\circ}$).

In this representation each atomic position is labelled in Z+1 different ways ($\underline{x}(\ell)$, $\underline{x}(\ell^1, \upsilon)$) and the identification of independent variables is difficult. We can, however, rewrite the model in terms of the bond vectors $\underline{a}_b$:

$$U = \frac{\alpha}{a^2}\sum_{b=1}^{N_B}\left(\underline{a}_b{}^2-a^2\right)^2 + \frac{\beta}{a^2}\sum_{<b,b^1>}\left(\underline{a}_b\cdot\underline{a}_b{}^1-a^2\,\mathrm{Cos}\theta\right)^2 \qquad 5.2$$

Here it is necessary to assign a direction to the bonds consistently, preferably keeping θ the same for each bond pair. This can only be achieved when all bonds at a given vertex have the same orientation with respect to that vertex.

Thus we have two types of vertex:



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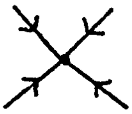


and each up vertex must be surrounded by down vertices, and vice versa. The ideal configuration is possible only in bipartite graphs, that is networks in which every closed cycle has an even number of bonds. The presence of odd rings forces some bonds to have a wrong orientation with respect to its neighbours. The lines threading odd rings are continuous (Rivier 1979) and the "wrong" bond pairs form walls bounded by these lines, as the unsatisfied bonds in an Ising spin glass form walls bounded by frustration lines. The unsatisfied bonds of a spin glass do, however, cost energy, whereas a wrong bond pair in the Keating model does not. It merely forces us to redefine θ for that particular bond pair (Fig. 5.1) as $\theta^1 = \Pi - \theta$ ($\mathrm{Cos}\,\theta^1 = -\mathrm{Cos}\,\theta$) and the bond bending term in equation 5.2 becomes:

$$U_B = \frac{\beta}{a^2} \sum_{<bb^1>} (|\underline{a}_b \cdot \underline{a}_b{}^1| - a^2 \mathrm{Cos}\ \theta)^2 \qquad 5.3$$

The energy is invariant under the discrete (Z_2) local transformation ($\underline{a}_b \rightarrow -\underline{a}_b$) and the position of the wrong bond pair can be moved around the ring by such a gauge transformation (Fig. 5.2).

The bond vectors ($\underline{a}_b$) are not independent variables because every ring in the network must close:

$$\sum_{b=1}^{r} (-1)^b \underline{a}_b = 0 \qquad 5.4$$

(here we assume that the orientation of the bonds alternate around the ring). The number of such constraints for any network (with N_A atoms, N_B bonds and a co-ordination number Z) is the number of independent cycles or cyclymatic number (c) given by

$$\begin{aligned} C &= N_B - N_A + 1 \\ &= (\tfrac{Z}{2} - 1)\, N_A + 1 \qquad 5.5 \end{aligned}$$

therefore the total number of degrees of freedom is

$$\begin{aligned} N &= 3 \times (N_B - C) \qquad 5.6 \\ &= 3\, (\tfrac{Z}{2} N_A - (\tfrac{Z}{2} - 1) N_A - 1) \qquad 5.7 \\ &= 3N_A - 3 \qquad 5.6 \end{aligned}$$

which is the dimensionality of the configuration space ($3N_A$) less the co-ordinates of the centre of mass (3).

The bond bending energy (equation 5.3) can also be written in an equivalent (at least in the harmonic approximation) form:

$$U_B = -\beta \sum_{<bb'>} \underline{a}_b^T \underline{\underline{J}}_{bb'} \underline{a}_{b'} \qquad 5.7$$

where $\underline{\underline{J}}_{bb^1}$ ϵ SO(3) represents a rotation of θ (or $\Pi - \theta$) about an axis perpendicular to the bonds $\underline{a}_b$ and $\underline{a}_{b^1}$ writing the angle between the bonds b and b^1 as

$\theta_{bb^1} = \theta + \epsilon_{bb^1}$ (or $\Pi - \theta + \epsilon_{bb^1}$) equation 5.7 becomes

$$U_B = -\beta \sum_{<bb^1>} a_b a_{b^1} \, \mathrm{Cos}\,(\theta_{bb^1} - \theta) \qquad 5.8$$

$$= -\beta \sum_{<bb^1>} a_b a_{b^1} \left(1 - \tfrac{1}{2}\epsilon^2_{bb^1} + O(\epsilon^4_{bb'})\right) \qquad 5.9$$

Similarly equation 5.3 becomes

$$U_B = \frac{\beta}{a^2} \sum_{<bb^1>} (a_b a_{b^1} \, \mathrm{Cos}\theta_{bb^1} - a^2 \, \mathrm{Cos}\theta)^2 \qquad 5.10$$

$$= \frac{\beta}{a^2} \sum_{<bb^1>} (a_b a_{b^1} \, \mathrm{Cos}\,(\theta + \epsilon_{bb^1}) - a^2 \, \mathrm{Cos}\theta)^2 \qquad 5.11$$

$$= \frac{\beta}{a^2} \sum_{<bb^1>} ((a_b a_{b^1} (\mathrm{Cos}\theta - \mathrm{Sin}\theta \epsilon_{bb^1} + O(\epsilon_{bb^1})^2)$$

$$-a^2 \mathrm{Cos}\theta)^2 \qquad 5.12$$

$$= \frac{\beta}{a^2} \sum_{<bb^1>} (a_b a_{b^1} - a^2) \mathrm{Cos}\theta - a_b a_{b^1} \mathrm{Sin}\theta \epsilon_{bb^1} +$$

$$O(\epsilon^2_{bb'}))^2 \qquad 5.13$$

In general the bond stretching force constant (α) is much larger than the bond bending force constant (β) and bond length deviations are a second order affect. Therefore, to a good approximation, we can set all bond lengths equal to a ($a_b = a_{b^1} = a$). Then, apart from an irrelevant constant and a rescaling of the force constant β, equation 5.13 is equivalent to 5.9.

The bond bending energy written in this way (equation 5.7) looks very similar to the generalized Edwards Anderson Model (equation 4.6) discussed in the previous chapter and it displays the same, continuous gauge invariance. Under a local rotation of the bond vector ($\underline{\underline{O}}_b \in SO(3)$)

$$\underline{a}_{b'} \to \underline{\underline{O}}_{b'} \, \underline{a}_b ; \quad \underline{a}_b^T \to \underline{a}_b^T \, \underline{\underline{O}}_b^T$$

and $\underline{\underline{J}}_{bb'} \to \underline{\underline{O}}_b \underline{\underline{J}}_{bb'} \, \underline{\underline{O}}_{b'}^T$

the energy remains unchanged. However the physical situation corresponds to $\underline{\underline{J}}_{bb'}$ representing a rotation of θ (or $\Pi - \theta$) about an axis perpendicular to the bonds $\underline{a}_b$ and $\underline{a}_{b'}$ and any realistic gauge transformation should preserve this property (just as the only physical rotations in a spin glass had magnitudes zero or Π). Here it is impossible to find a set of rotations to satisfy this constraint when the co-ordination number is greater than two. Thus, although the bond vectors $\underline{a}$ are dynamical variables, the J's are quenched for any particular configuration. Moreover the ring closure constraint is not gauge invariant.

The interaction matrices ($\underline{\underline{J}}_{bb'}$.) play the role of connections, relating the local bond direction of one bond to the minimum energy direction of a neighbouring bond. The bond vectors are defined at sites on the mid points of the bonds on the original network and the connections are defined on the links between these sites. Thus we have a new network (co-ordination number $\frac{Z}{2}(Z-1)$) which is actually the star transformation of the original network (Fig. 5.3). We can define a second rotation matrix $\underline{\underline{R}}_{bb'}$ on the links which relates the actual direction of the bonds b and b' (Fig. 5.4):

$$\underline{a}_{b'} = \underline{\underline{R}}_{b'b}\,\underline{a}_b \quad \text{or} \quad \underline{a}_b = \underline{\underline{R}}_{bb'}\,\underline{a}_{b'} \qquad 5.14$$

Again the rotation is defined about an axis perpendicular to the bonds $\underline{a}_b$ and $\underline{a}_{b'}$. As before the combined rotation ($\underline{\underline{J}}_{bb'}\ \underline{\underline{R}}^{-1}_{b'b}$) is small and we can expand it in terms of an infinitesimal, antisymmetric matrix ($ga\ \underline{\underline{A}}_{bb'}$)

i.e $\underline{\underline{J}}_{bb'}\,\underline{\underline{R}}^{-1}_{bb} \doteq e^{ga\,\underline{\underline{A}}_{bb'}} = \mathbb{1} + ga\ \underline{\underline{A}}_{bb'} + O(g^2)$ 5.15

Thus the variables $\underline{\underline{A}}_{bb'}$ can be regarded as the fields in a continuous random network model of glass and the energy can be written in terms of this field (section 5.4). There are, however, constraints imposed on these fields, equivalent to the ring closure constraints on the bond variables (equation 5.4). No such additional constraints were needed in the spin glass model where the rings were naturally closed.

5.3 Defects and Constraints

We saw in the previous chapter that quenching the interactions in a spin glass had the effect of imposing constraints on the field variables. The analogous effect occurs in a covalent glass because the ordered product of $\underline{\underline{J}}$ around a closed contour is not, in general, equal to the identity. However., for any real configuration the ordered product of $\underline{\underline{R}}$ around a closed contour must return the bond to its original direction and once again the curvature of the modified gauge field ($\tilde{A}$) equals the lattice curvature:

i.e $$\mathbb{1} - \prod_{\alpha\varepsilon R} e^{ga\tilde{A}.\alpha} = \mathbb{1} - \prod_{\alpha\varepsilon R} \underline{\underline{J}}_{\alpha} = \mathcal{G}_R \tag{5.16}$$

$$\begin{aligned}\tilde{A}_{\alpha} &= (J_{12}J_{23}\cdots J_{\ell-1,\ell})\underline{A}_{\alpha}(J_{12}J_{23}\cdots J_{\ell-1,\ell})^{-1}\\ &= (\prod_{\beta<\alpha} \underline{\underline{J}}_{\beta})\ \underline{\underline{A}}_{\alpha}\ (\prod_{\beta<\alpha} \underline{\underline{J}}_{\beta})^{-1}\end{aligned} \tag{5.17}$$

and $\prod_{\beta<\alpha}$ represents the ordered product along the links (β) of the ring (R). In a covalent network one would expect the curvature to be small, unlike the spin glass in which frustration lines are associated with rotations of Π.

A more significant constraint in a continuous random network is that of ring closure, represented by equation 5.4. A ring of bonds in a relaxed configuration (with $\underline{\underline{A}}_{\alpha} = 0$ on all links) may not, in fact, close and the vector joining the initial and final points of the relaxed ring ("cut" on the link between the first bond (g^1) and the ℓth bond) is given by:

$$\Delta\underline{B}_R = \underline{a}_1 - \underline{\underline{J}}_{21}\,\underline{a}_1 + \underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{a}_1 - \ldots.(-1)^{\ell-1}\,\underline{\underline{J}}_{\ell,\ell-1}\ldots.$$

$$\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\,\underline{a}_1 = a_{-1} + [\Sigma^{\ell-1}_{\alpha^1=1}\,(\Pi^1_{\beta^1=\alpha^1-1}\,(-\underline{\underline{J}}_{\beta^1}))]\,\underline{a}_1 \qquad 5.18$$

$\Pi^1_{\beta^1=\alpha-1}$ indicates the ordered product along the links β^1 (directed from i+1 to i) from α -1 (=ℓ , ℓ-1) to 1(=2,1). We have assumed that the orientation of the bonds alternate around the ring, therefore the ℓ'th bond of an odd ring will have the wrong orientation with respect to the first bond. From equation 5.4

$$\underline{a}_1 - \underline{\underline{R}}_{21}\,\underline{a}_1 + \underline{\underline{R}}_{32}\underline{\underline{R}}_{21}\underline{a}_1 - \ldots.(-1)^{\ell-1}\,\underline{\underline{R}}_{\ell,\ell-1}\ldots\underline{\underline{R}}_{32}\underline{\underline{R}}_{21}$$

$$\underline{a}_1 = 0 \qquad 5.19$$

therefore $(\mathbb{1}-\underline{\underline{R}}_{21}\underline{\underline{J}}^{-1}_{21}\underline{\underline{J}}_{21} + (\underline{\underline{R}}_{32}\underline{\underline{J}}^{-1}_{32})\,\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{\underline{J}}^{-1}_{21}(\underline{\underline{R}}_{21}\underline{\underline{J}}^{-}_{21})\,\underline{\underline{J}}_{21}$

$$-(\underline{\underline{R}}_{43}\underline{\underline{J}}^{-1}_{43})\,\underline{\underline{J}}_{43}\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{\underline{J}}^{-1}_{21}\,J^{-1}_{32}(\underline{\underline{R}}_{32}\underline{\underline{J}}^{-1}_{32})\,\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{\underline{J}}^{-1}_{21}$$

$$(\underline{\underline{R}}_{21}\underline{\underline{J}}^{-1}_{21})\underline{\underline{J}}_{21}+\ldots.\quad)\underline{a}_1 = 0 \qquad 5.20$$

or $(\mathbb{1}-(\mathbb{1}+ga\underline{\underline{A}}_{21})^{-1}\underline{\underline{J}}_{21} + (\mathbb{1}+ga\underline{\underline{A}}_{32})^{-1}\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{\underline{J}}^{-1}_{21}(\mathbb{1}+ga\underline{\underline{A}}_{21})^{-1}\underline{\underline{J}}_{21}$

$$-(\mathbb{1}+ga\underline{\underline{A}}_{43})^{-1}\underline{\underline{J}}_{43}\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{\underline{J}}^{-1}_{21}\,\underline{\underline{J}}^{-1}_{32}\,(\mathbb{1}+ga\underline{\underline{A}}_{32})^{-1}\underline{\underline{J}}_{32}\underline{\underline{J}}_{21}\underline{\underline{J}}^{-1}_{21}$$

$$(\mathbb{1}+ga\underline{\underline{A}}_{21})^{-1}\underline{\underline{J}}_{21}+\ \ldots\quad)\underline{a}_1 = 0 \qquad 5.21$$

Using $\underline{\underline{J}}_{ij} = \underline{\underline{J}}^{-1}_{ji}$ and $(\mathbb{1}+ga^1\underline{\underline{A}}_{21})^{-1} = (\mathbb{1}+ga^1\underline{\underline{A}}_{12})$ this becomes $(\mathbb{1}-\underline{\underline{J}}_{21}+\underline{\underline{J}}_{32}\underline{\underline{J}}_{21} - \underline{\underline{J}}_{43}\underline{\underline{J}}_{32}\underline{\underline{J}}_{21} + \ldots(-1)^{\ell}\,\underline{\underline{J}}_{\ell,\ell-1}$

$$\ldots\underline{\underline{J}}_{32}\underline{\underline{J}}_{21} + ga^1(-\underline{\underline{J}}^{-1}_{12}\,\tilde{A}_{12} + \underline{\underline{J}}^{-1}_{23}\underline{\underline{J}}^{-1}_{12}(\tilde{A}_{12}+\tilde{A}_{23}) - \underline{\underline{J}}^{-1}_{34}\underline{\underline{J}}^{-1}_{23}$$

$$\underline{\underline{J}}^{-1}_{12}(\tilde{A}_{12}+\tilde{A}_{23}+\tilde{A}_{34})+\ldots\underline{\underline{J}}^{-1}_{\ell-1,\ell}\ \ldots\underline{\underline{J}}^{-1}_{23}\underline{\underline{J}}^{-1}_{12}(\tilde{A}_{12}+\tilde{A}_{23}+\ldots$$

$$\tilde{A}_{\ell-1,\ell}\ ))+0(g^2))\underline{a}_1=0 \qquad 5.22$$

Substituting this value for $\Delta\underline{B}_R$ in 5.18 this becomes

$$ga \sum_{\alpha=1}^{\ell-1} [(\prod_{\beta=1}^{\alpha} -J_\beta)^{-1}[\sum_{\beta=1}^{\alpha} \tilde{A}_\beta]] \underline{a}_i = -\Delta\underline{B}_R \qquad 5.23$$

Equation 5.23 replaces 5.4 as the relevant constraints of the $\tilde{A}$ field. Alternatively we can write equation 5.18 as

$$\Delta\underline{B}_R = ga\, \underline{\underline{T}}_R\, \underline{a}_i \qquad 5.24$$

where $\underline{\underline{T}}_R \doteq \frac{1}{ga} (\mathbb{1} + \sum_{\alpha'=1}^{\ell-1} (\prod_{\beta'=\alpha'-1}^{1} (-J_{\beta'})))$ 5.25

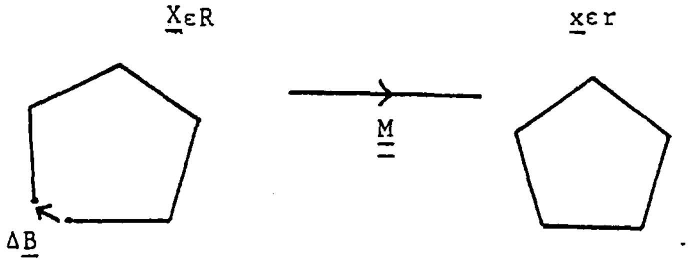
then equation 5.23 becomes

$$\sum_{\alpha=1}^{\ell-1} [(\prod_{\beta=1}^{\alpha} (-J_\beta))^{-1}(\sum_{\beta=1}^{\alpha} \tilde{A}_\beta)] = \underline{\underline{T}}_R \qquad 5.26$$

$\underline{\underline{T}}$ is fixed for any particular configuration of J's and thus for any given network structure.

The situation in which closed rings of bonds in a real configuration do not close in a relaxed configuration also arises in crystals, where it is due to the presence of dislocations. In fact the density of dislocations in a crystal can be directly related to the torsion of a non-Euclidean space, the geometry of which is derived from a mapping between the actual configuration and the stress free (relaxed) configuration (Bilby et al 1955).

A similar argument can be invoked for glasses but the torsion here is related to the closure failure of the ring ($\Delta\underline{B}$). A mapping $\underline{\underline{M}}$ is defined between vectors in the real configuration (r) (in which the ring is closed) and vectors in the relaxed configuration (R).



$$d\underline{X}^K = M^K{}_k{}^{-1} \; d\underline{x}^k \qquad 5.27$$

In the presence of curvature such a mapping is path dependent and cannot be uniquely defined everywhere. It can, however, always be defined along a path if the value $(\underline{\underline{M}}o)$ at the start of the path $(\underline{x}o)$ is known. The mapping is related to the connection (Γ^i_{jk}) which defines parallel transport in the real configuration by:

$$\Gamma^i_{jk} = M^i{}_K \, \partial_k \; M^K{}_j{}^{-1} \qquad 5.28$$

The integral of $d\underline{X}$ along an arbitrary closed contour in R must, by definition, be zero therefore the opening vector can be written in terms of the contour integral of the mapping as follows:

$$\oint_{\mathrm{in}R} d\underline{X}^K = 0 = \oint_{\mathrm{in}r} M^K_k \; dx^k - \Delta B^K \qquad 5.29$$

and the opening vector can also be defined in the space r by defining the inverse mapping:

$$\Delta b^{k} = M^{k}_{K} \oint_{inr} M^{-1\,K}{}_{j}\, dx^{j} \qquad 5.30$$

Using Stoke's Theorem to relate the contour integral to a surface integral this becomes:

$$\Delta b^{k} = M^{k} \int_{S} (\partial_{i} M^{-1\,K}{}_{j} - \partial_{j} M^{-1\,K}{}_{i})\, dS^{ij} \qquad 5.31$$

$$= \int_{S} (\Gamma^{k}_{ij} - \Gamma^{k}_{ji})\, dS^{ij} \qquad 5.32$$

$$= \int_{S} T^{k}_{ij}\, dS^{ij} \qquad 5.33$$

Here T^{k}_{ij} is defined as the antisymmetric part of the connection. It is, in fact, Cartan's Torsion of Differential geometry (Cartan 1928) and it is related to the closure failure of parallelograms in a non-Euclidean space.

As it stands our model is inherently discrete, with the mapping defined only on the bonds, therefore Stoke's Theorem cannot be applied in Equation 5.30. However in a continuum model with a geometry defined by a mapping from a local stress free configuration onto the actual configuration, the ring closure constraints can be included by quenching the torsion and curvature of the geometry. This will be done in the next chapter.

5.4 The Keating Model and the Gauge Fields

In section 5.2 we showed that the bond bending term of the Keating model could be written as:

$$U_B = -\beta \sum_{<bb'>} \underline{a}_b^T \; \underline{\underline{J}}_{bb'} \; \underline{a}_{b'}$$

Following the same procedure as for spin glass (equations 4.12 to 4.17) we can write this as:

$$U_B = \beta a^2 a'^2 \; g^2 \sum_{<bb'>} \mathrm{Tr}\,(\underline{\underline{A}}_{bb'}^2) \qquad 5.34$$

Here a is the bond length and a' is a length typical of the links on the star network (Fig. 5.3).

Bond stretching is, geometrically, a second order effect because, for $\alpha >> \beta$, the bond length can be regarded as constant. Bond stretching may, however, make a significant contribution to the energy, because of the large force constant, and we can include it in the above formalism by redefining the $\underline{\underline{J}}$ matrix to include a small scaling factor:

i.e. $|\underline{\underline{J}}_{b'b} \, \underline{a}_b|^2 = a^2$ 5.35

$\underline{\underline{R}}_{bb}^{'}$ is defined as before but now

$\underline{\underline{J}}_{b'b} \, \underline{\underline{R}}_{b'b}^{-1} = \mathbb{1} + g a' \, \underline{\underline{A}}_{b'b}$ is not a pure rotation and $\underline{\underline{A}}_{b'b}$ has a small diagonal component $(\frac{\lambda b}{g a'} \; \mathbb{1})$

with $\lambda_b = \frac{a_b}{a} - 1$

Now the bond stretching energy

$$U_S = \frac{\alpha}{a^2} \sum_b (a_b^2 - a^2)^2 \qquad 5.36$$

$$= \alpha a^2 \sum_b \left(\frac{a_b^2}{a^2} - 1\right)^2 \qquad 5.37$$

$$= \alpha a^2 \sum_b (\lambda_b^2 + 2\lambda_b)^2 \qquad 5.38$$

$$= 4\alpha \quad a^2 \sum_b \lambda_b^2 + O(\lambda_b^3) \qquad 5.39$$

$$= \frac{4\alpha g^2 a^{1\,2} a^2}{9 \quad \frac{Z}{2}(z-1)} \sum_{<bb^1>} (\mathrm{Tr}\ \underline{\underline{A}}_{bb^1})^2 \qquad 5.40$$

$$= \alpha^1 g^2 \ a^{1\,2} a^2 \sum_{<bb^1>} (\mathrm{Tr}\ \underline{\underline{A}}_{bb^1})^2 \qquad 5.41$$

where α^1 is a rescaled force constant. Thus the Keating model for the potential energy of covalent glasses can be written in terms of an over complete set of gauge variables ($\underline{\underline{A}}_{bb^1}$) defined on the links joining the bonds of the original network:

$$U = g^2 a^2 a^{1\,2} \sum_{<bb^1>} [\alpha^1 (\mathrm{Tr}\ \underline{\underline{A}}_{bb^1})^2 + \beta^1\ \mathrm{Tr}(\underline{\underline{A}}^2_{bb^1})] \qquad 5.42$$

Constraints, which take the form of quenched curvature and torsion, must be imposed on the fields and such constraints act as sources of the field ($\underline{\underline{A}}_{bb^1}$) and increase the energy with respect to a crystal. They can therefore be regarded as the intrinsic defects of a covalent glass.

The energy of a glass (equation 5.42) closely resembles that of a spin glass (equation 4.17) and we might attempt to derive a continuum formalism as before. There is, however, one significant difference, in that the links along which the gauge variables are defined (b, b^1) are orientated in random directions in space and not (as in the spin glass model) along the well defined directions of the bonds on a simple cubic lattice. This, in fact, inhibits the transition to the continuum as there is no unique method of assigning the spacial directions (μ) to the connections ($\underline{A}$). It is necessary, therefore, to approach the continuum from a macroscopic point of view, in which each element of space contains many atoms. We consider this approach in the next chapter and include the torsion and curvature of the underlying network as constraints in the continuum model.

5.5 Conclusions

In this chapter we considered a representation of the Keating model in which the gauge invariance was evident. The model is, in some respects, similar to the spin glass model considered in chapter 4 but in addition to the curvature constraints a covalent glass also has ring closure constraints which can be included as torsion of the rings. We did not, however, succeed in finding the continuum limit for this model, because of the absence of an underlying lattice on which the gauge variables were defined.

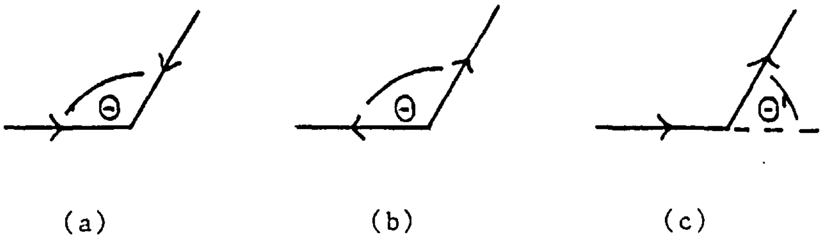


Fig. 5.1

The bonds in (a) and (b) are correctly orientated with respect to each other but (c) is not. The equilibrium angle in this case is $\theta^1 = \Pi - \theta$.

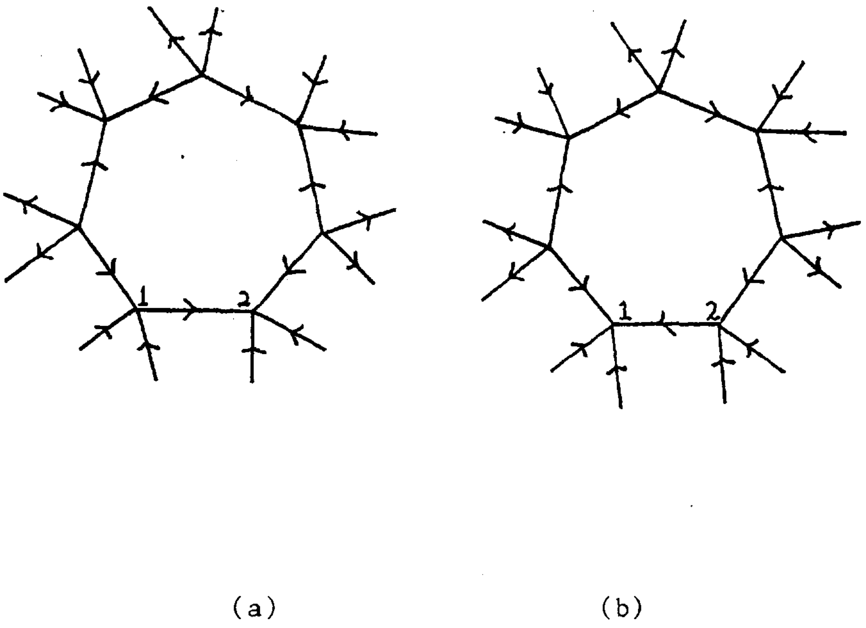


Fig. 5.2

The position of the "wrong" bond pairs are moved from vertex 1 to vertex 2 by the local transformation.

$\underline{a}_{12} \rightarrow -\underline{a}_{12}$

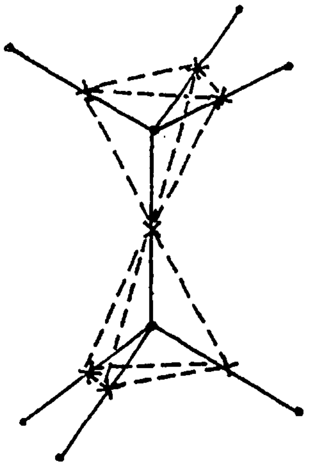


Fig. 5.3

Star transformation of a network

. - Vertices of original network

_ - Bonds of original network

x - Vertices of star transformed network

--- Bonds of star transformed network

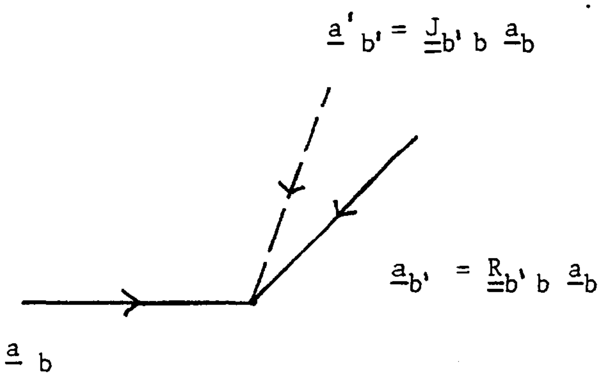


Fig. 5.4

$\underline{a}_b$, $\underline{a}_{b^1}$, are the actual directions of the bonds b and b^1. $\underline{a}^1_{b^1}$ is the minimum energy configuration of bond b^1 with respect to $\underline{a}_b$; $\underline{a}^1_{b^1}$ is coplanar with $\underline{a}_b$ and $\underline{a}_{b^1}$.

CHAPTER 6

A CONTINUOUS FIELD THEORY OF GLASS

6.1 Introduction

On a macroscopic level, when all relevant length scales are much longer than the interatomic distance, a glass is essentially an isotropic elastic continuum with internal stresses. The isotropic nature arises from the randomness, because all spacial directions are equivalent, and the internal stresses are due to the structure of the underlying network of the glass in which constraints (in particular ring closure) are imposed on the field variables (the bond vectors) and prevent them from relaxing to the minimum energy configuration. Thus the torsion and curvature of the discrete model (chapter 5) survive the averaging procedure and are present as sources of stress and strain in the isotropic elastic continuum.

A glass, when viewed at this level, is thus indistinguishable from a crystalline continuum with a distribution of sources of internal stress (dislocations) but there are two important differences. The distant parallelism (zero curvature) constraint introduced by some authors (Kondo 1953, Bilby et al 1955) to describe crystalline dislocations must be absent in glasses, because there is no underlying lattice. In addition the torsion and curvature of a glass are present at all temperatures even in the "ground state". They cannot be eliminated by annealing because they are an intrinsic property of the underlying structure of the glass. This model is not, however, equivalent to the model of a glass as a heavily dislocated crystal, suggested by Cotterill et al (1974). Here the reference state is the stress free configuration and does not, on any scale, resemble the crystalline structure.

In this chapter we summarize the relevant features of the continuum theory of dislocations and demonstrate how this leads naturally to an expression for the energy of the intrinsic defects (torsion and curvature) of glass. Thermally excited dislocations tend to screen the interaction between intrinsic defects. Low energy tunnelling excitations, which have the effect of reversing the direction of a small, intrinsic defect loops, play the role of the two level system in this model. Topologically stable defects, in the form of 2π disclinations, are present at high temperatures and their interaction energy is screened by dislocations in such a way that they interact via a $1/r$ potential.

6.2 Field Theory of an Elastic Continuum with Torsion and Curvature

The relationship between differential geometry and a crystal with dislocations was first pointed out by Kondo (1953) and Bilby et al (1955) and since then the subject has been extensively studied by several authors (Kröner (1955), (1960); Seeger (1961)). The following discussion is closely related to those of Kröner (1980) and Lardner (chapter 7).

The starting point for a differential geometry description of an elastic continuum with sources of internal stress is a mapping ($\underline{\underline{M}}$) between the local stress free configuration (natural state) and the actual configuration. The local reference or stress free state is the configuration in which the stresses are relaxed in a small neighbourhood of the point under consideration. An orthonormal triad of vectors $\{\underline{U}^K\}$ ($K = 1,2,3$) is mapped from the local reference on to a triad in the actual configuration $\{\underline{e}^k\}$ by an operator $\underline{\underline{M}}$ (Figure 6.1) defined by:

$$\underline{e}^k = M^k{}_K \, \underline{U}^K \qquad 6.1$$

$$\underline{u}^K = M^{K^{-1}}{}_k \, \underline{e}^k \qquad 6.2$$

The metrics (g^{KL} and g^{kl}) of the reference state and actual configuration can be written in terms of these basis vectors:

$$g^{KL} = \underline{U}^K \cdot \underline{U}^L = \delta^{KL} \qquad 6.3$$

$$g^{k\ell} = \underline{e}^k \cdot \underline{e}^\ell \qquad 6.4$$

As before, capital letters ($\underline{X}$) label positions in the reference configuration and $\underline{x}$ labels positions in the actual configuration. The mapping can be defined consistently along a continuous path by considering points with overlapping neighbourhoods, and ensuring that the reference triads in such neighbourhoods are parallel. However, in the presence of curvature, a mapping defined in this way may not have the same value at the start and finish of a closed path. Thus $\underline{\underline{M}}$ is path dependent but the connection (Γ) derived from the mapping is not path dependent and it can be defined uniquely at all points of space.

$$\Gamma^{k}_{ij} = M^{k}_{K} \, \partial_j \, M^{K^{-1}}_{i} \qquad 6.5$$

The connection defines parallel transport in the actual configuration as the change in the vector $\underline{V}$ caused by parallel transport along the actual path $d\underline{x}$ is

$$dV^k = -\Gamma^{k}_{ij} \, V^i \, dx^j \qquad 6.6$$

The torsion ($T_{ij}{}^{k}$) and curvature ($R_j{}^{ikl}$) are related to the connection by:

$$T_{ij}^{\ \ k} = \tfrac{1}{2}\left(\Gamma^{k}_{ij} - \Gamma^{k}_{ji}\right) \qquad 6.7$$

and $$R_{j\ kl}^{\ i} = \partial_k \Gamma^{i}_{jl} - \partial_l \Gamma^{i}_{jk} + \Gamma^{i}_{mk}\Gamma^{m}_{jl} - \Gamma^{i}_{ml}\Gamma^{m}_{jk} \qquad 6.8$$

The tensors $T_{k\ell}^{\ \ n}$ and $R_{j\ k\ell}^{\ i}$ are antisymmetric in the indices k and ℓ. For metric spaces $R_{ijkl} = g_{jh}R_{i\ kl}^{\ h}$ is also antisymmetric in i and j therefore it is convenient to define the dual tensors:

$$T^{in} = \tfrac{1}{2}\,\epsilon^{ikl}\,T_{kl}^{\ \ n} \qquad 6.9$$

and $$R^{pn} = \tfrac{1}{4}\,\epsilon^{pij}\,\epsilon^{nkl}\,R_{ijkl} \qquad 6.10$$

The identities of differential geometry give us continuity equations for the torsion and curvature:

$$(D_i + 2T_{ij}^{\ \ j})R^{ki} = 0 \qquad 6.11$$

$$(D_i + 2T_{ij}^{\ \ j})\,T^{i}_{\ k} = \epsilon_{ilk}R^{il} \qquad 6.12$$

Equation 6.11 is the Bianchi Identity for a geometry with torsion and 6.12 is the torsion or second identity (Schouten 1954). Di is the usual covariant differential operator:

$$D_iV^k = \partial_iV^k + \Gamma^{k}_{mi}\,V^m \qquad 6.13$$

In the absence of curvature equation 6.12 is the conservation law for the density of dislocations (T^{in}). Curvature is generally associated with disclinations, thus De Witt (1970) has interpreted equation 6.12 to mean that dislocations can end on disclinations.

The energy density ($U(\underline{x})$) of an elastic medium is the product of the strain tensor (E_{ij}) and the stress tensor (σ_{ij}) and these (symmetric) tensors are related by the elastic modulus tensor $C_{ij}{}^{kl}$:

$$U(\underline{x}) = \sigma_{ij}(\underline{x})\, E^{ij}(\underline{x}) \qquad 6.14$$

$$\sigma_{ij} = C_{ij}{}^{kl}\, E_{kl} \qquad 6.15$$

Equations 6.14 and 6.15 are correct only in the linear approximation (to first order in the strain field) but they are sufficient for most applications. The internal strain field of glass will, in general, be small enough for the linear equations to be valid. This introduces a number of simplifications, in particular the metric of the actual configuration (g^{ij}) becomes δ^{ij} because deviations from the orthogonal configurations are of the order of the strain field. There is, therefore, no distinction between covariant and contravariant components of tensors. For an isotropic medium (such as a glass) the tensor C_{ijkl} can be written in terms of two Lamé constants λ, μ:

$$C_{ijkl} = \lambda \delta_{ij}\delta_{kl} + \mu(\delta_{ik}\ \delta_{jl} + \delta_{il}\ \delta_{jk}) \qquad 6.16$$

We must also include the equilibrium condition for an elastic continuum, in the absence of body forces:

$$\partial_i \sigma_{ij} = \partial_j \sigma_{ij} = 0 \qquad 6.17$$

Equations 6.14 to 6.17 constitute a field theory of an elastic continuum. The parameters (σ_{ij}, E_{ij}) are related to the differential geometry approach through the strain tensor, which is a measure of the difference between the length scales in the reference configuration ($ds^2 = g_{kl}\, dx^k dx$) and the actual configuration ($dS^2 = g_{KL}\, dX^K dX^L$)

$$\text{i.e. } ds^2 - dS^2 = g_{kl}\, dx^k dx^l - g_{KL}\, dX^K dX^L \qquad 6.18$$

$$= g_{kl}\, dx^k dx^l - g_{KL}\, M^{K^{-1}}{}_{k}\, M^{L^{-1}}{}_{l}\, dx^k dx^l \qquad 6.19$$

$$= 2E_{kl}\, dx^k dx^l \qquad 6.20$$

$$\text{therefore} \qquad E_{kl} = \tfrac{1}{2}(g_{kl} - g_{KL}\, M^{-1K}{}_{k}\, M^{\overset{-1}{L}}{}_{l}) \qquad 6.21$$

Torsion and curvature are introduced via the strain incompatibility tensor η_{ij} defined by:

$$\eta_{ij} = -\varepsilon_{ipr}\, \varepsilon_{jqs}\, \partial^p \partial^q E^{rs} \qquad 6.22$$

and, in the linear approximation, this is given by:

$$\eta_{ij} = -[\varepsilon_{ipr}\, \partial^p T^r{}_j + R_{ij}]\text{symmetric} \qquad 6.23$$

The proof of this result is outlined in Appendix 1.

The problem of finding the elastic energy of a medium in the presence of strain incompatibility has been solved by Kröner (1955) who introduced a symmetric stress function tensor χ_{ij}, defined by:

$$\sigma_{ij} = -2\mu[\epsilon_{ikm}\, \epsilon_{jln}\, \partial_k \partial_l\, (\chi_{mn} + \frac{\upsilon}{1-\upsilon}\, \delta_{mn}\, \chi_{pp})] \qquad 6.24$$

with $\upsilon = \frac{\lambda}{2\ (\lambda+\mu)}$ (Poisson's Ratio)

A stress tensor of this form automatically satisfies equation 6.17. This definition of χ in equation 6.24 is, however, somewhat ambiguous as any tensor of the form

$$\overset{o}{\chi}_{ij} = \partial_i\, U_j + \partial_j U_i \qquad 6.25$$

can be added to the stress function without changing the stress. This is analogous to the ambiguity in the definition of the vector potential $\underline{A}$ from the magnetic induction ($\underline{B} = \underline{\nabla} \times \underline{A}$) in electromagnetism. The stress and strain tensors are, in fact, invariant under the gauge transformation: $\chi_{ij}{}^1 = \chi_{ij} + \partial_i U_j + \partial_j U_i$ 6.26

The equations are simplified considerably if we work in the "Coulomb" Gauge:

$$\partial_j\, \chi_{ij} = \partial_i\, \chi_{ij} = 0 \qquad 6.27$$

For any symmetric tensor Sij

$$\epsilon_{mki}\, \epsilon_{n\ell j}\, \partial_k \partial_\ell\, S_{ij} = (\nabla^2\, S_{kk} - \partial_j \partial_k\, S_{jk})\, \delta_{mn}$$

$$+\ \partial_m \partial_k\, S_{nk} + \partial_n \partial_k\, S_{mk} - \nabla^2 S_{mn} - \partial_m \partial_n\, S_{kk} \qquad 6.28$$

therefore, in the Coulomb Gauge equation 6.24 becomes

$$\sigma_{ij} = -2\mu\ \ [\nabla^2 \chi_{kk}\, \partial_{ij} - \nabla^2 \chi_{ij} - \partial_i \partial_j\, \chi_{kk}$$

$$+\ \frac{\upsilon}{1-\upsilon}\, (2\nabla^2\, \chi_{kk} \partial_{ij} + 2\, \partial_i \partial_j\, \chi_{kk}$$

$$-\nabla^2\, \chi_{kk} \delta_{ij} - 3 \partial_i \partial_j\, \chi_{kk})] \qquad 6.29$$

$$= 2\mu\ [\nabla^2\chi_{ij} - \frac{1}{1-\upsilon}(\nabla^2\chi_{kk}\delta_{ij} - \delta_i\partial_j\ \chi_{kk})] \qquad 6.30$$

Inverting equation 6.15 leads to

$$E_{ij} = \frac{1}{2\mu}\sigma_{ij} - \frac{\upsilon}{2\mu(1+\upsilon)}\delta_{ij}\sigma_{kk} \qquad 6.31$$

$$=\nabla^2\chi_{ij} - \frac{1}{1-\upsilon}(\nabla^2\chi_{kk}\delta_{ij} - \partial_i\partial_j\ \chi_{kk})$$

$$- \frac{\upsilon}{1+\upsilon}(\delta_{ij}\nabla^2\chi_{kk} - \frac{1}{1-\upsilon}\delta_{ij}(3\nabla^2\chi_{kk} - \nabla^2\chi_{kk})) \qquad 6.32$$

$$\text{therefore } E_{ij} = \nabla^2\chi_{ij} - \nabla^2\chi_{kk}\ \delta_{ij} + \frac{1}{1-\upsilon}\partial_j\partial_i\chi_{kk} \qquad 6.33$$

$$\text{and} \quad \eta_{ij} = -[(\nabla^2E_{kk} - \partial_k\partial_1\ E_{kl})\delta_{ij} + \partial_i\partial_k\ E_{kj} + \partial_j\partial_k\ E_{ki}$$

$$- \nabla^2E_{ij} - \partial_i\partial_j\ E_{kk}] \qquad 6.34$$

becomes (in the Coulomb gauge):

$$\eta_{ij} = -[(\nabla^2\nabla^2\chi_{kk}\delta_{ij} - \nabla^2\nabla^2\chi_{ij} - \nabla^2\partial_i\partial_j\ \chi_{kk})$$

$$- (3\nabla^2\nabla^2\chi_{kk}\delta_{ij} - \nabla^2\nabla^2\ \chi_{kk}\delta_{ij} + 2\partial_i\partial_j\nabla^2\chi_{kk} - \nabla^2\nabla^2$$

$$\chi_{kk}\delta_{ij}$$

$$- 3\nabla^2\partial_i\partial_j\ \chi_{kk}) + \frac{1}{1-\upsilon}(\nabla^2\nabla^2\chi_{kk}\delta_{ij} - \partial_k\partial_\ell\partial_k\partial_\ell\chi_{pp}\delta_{ij}$$

$$+2\partial_i\partial_k\partial_j\partial_k\ \chi_{pp} - \nabla^2\partial_i\partial_j\ \chi_{pp} - \partial_i\partial_j\partial_k\partial_k\ \chi_{pp})] \qquad 6.35$$

$$\text{or} \qquad \eta_{ij} = \nabla^2\nabla^2\ \chi_{ij} \qquad 6.36$$

Here $\nabla^2\nabla^2$ (or ∇^4) represents the biharmonic operator

$$\partial_k\partial_k\partial_\ell\partial_\ell$$

The internal energy can now be written in terms of the stress function:

$$U = \int d^3\underline{x} \quad \sigma_{ij}(\underline{x}) \; E_{ij}(\underline{x}) \qquad 6.37$$

$$= -2\mu \int d^3\underline{x} \; \varepsilon_{ikm} \; \varepsilon_{jln} \; \partial_k \partial_l \; (\chi_{mn}(\underline{x}) + \frac{\upsilon}{1-\upsilon} \delta_{mn} \chi_{pp}(\underline{x})) \; E_{ij}(\underline{x}) \qquad 6.38$$

After integrating by parts and dropping surface terms we have:

$$U = -2\mu \int d^3\underline{x}(\chi_{mn}(\underline{x}) + \frac{\upsilon}{1-\upsilon} \; \delta_{mn} \; \chi_{pp}(\underline{x}))\varepsilon_{ikm}\varepsilon_{jln}\partial_k\partial_l E_{ij} \qquad 6.39$$

$$= 2\mu \int d^3\underline{x} \; (\chi_{mn}(\underline{x}) + \frac{\upsilon}{1-\upsilon} \; \delta_{mn} \; \chi_{pp}(\underline{x})) \; \eta_{mn}(\underline{x}) \qquad 6.40$$

$$= 2\mu \int d^3\underline{x} \; (\chi_{mn}(\underline{x}) + \frac{\upsilon}{1-\upsilon} \; \delta_{mn} \; \chi_{pp}(\underline{x})) \; \nabla^4\chi_{mn}(\underline{x}) \qquad 6.41$$

The solution of equation 6.36 (see, for example, Lardner p.280), with the boundary condition that $\chi_{ij} = 0$ at infinity, is

$$\chi_{ij}(\underline{x}) = -\frac{1}{8\Pi} \int d^3\underline{x}^1 \quad \eta_{ij}(\underline{x}^1) \quad |\underline{x}-\underline{x}^1| \qquad 6.42$$

therefore the internal energy of an elastic continuum with incompatibility $\eta(\underline{x})$ is

$$U = -\frac{\mu}{4\Pi} \int d^3\underline{x}\int d^3\underline{x}^1(\eta_{mn}(\underline{x}) + \frac{\upsilon}{1-\upsilon} \; \eta_{kk}(\underline{x})\delta_{mn})|\underline{x}-\underline{x}^1| \; \eta_{mn}(\underline{x}^1) \qquad 6.43$$

All results in this section are classical (Lardner ch.7, Nabarro Ch.2).

6.3 Field Theory of Glass

The above discussion is valid for any isotropic elastic continuum with sources of internal stress, hence we can apply it directly to glasses. The field variable is the symmetric tensor (χ_{ij}) and this must satisfy the constraints imposed by the incompatibility (equation 6.36). The structure of the discrete network underlying the elastic continuum in a glass is such that there is a finite torsion and curvature quenched into the system and, unlike the crystalline case, this cannot be eliminated by annealing. It is, in fact, an intrinsic property of the glass. The quenched torsion and curvature combine (as in equation 6.23) to form the quenched incompatibility tensor (η^Q) and, from the definition (equation 6.22) this must satisfy the continuity equations:

$$\partial_i \eta_{ij}^Q = \partial_j \eta_{ij}^Q = 0 \qquad 6.44$$

The continuity equations imply that the intrinsic defects (η_{ij}^Q) take the form of lines which cannot end within the medium.

We can write the partition function for a glass in terms of a functional integral over all configurations of the field (χ) which satisfy the constraints imposed by η^Q:

$$Z=\int D\chi \; (\exp -2\beta\mu\int d^3\underline{x}(\chi_{mn}(\underline{x})+\frac{\upsilon}{1-\upsilon}\;\delta_{mn}\chi_{pp}(\underline{x}))\nabla^4\chi_{mn}(\underline{x})))$$

$$\delta(\eta_{ij}^Q(\underline{x}) - \nabla^4 \chi_{ij}(\underline{x})) \qquad 6.45$$

This equation has a similar form to equation 4.33 for the partition function of a spin glass and, again, constraints are imposed on the fields by the intrinsic defects or, equivalently, the structure of the underlying network. The interaction energy calculated from this functional integral is that given by equation 6.43 (with η^Q replacing η) however equation 6.45 is not a realistic description of the thermodynamics of a glass because it excludes the possibility of thermal fluctuations of the incompatibility. Such fluctuations occur via the creation of small dislocation loops, a process which is possible in any elastic continuum, and (unlike crystalline dislocations) the Burger's vector of dislocations in a glass is not quantized because there is no underlying symmetry which must be respected. This is a manifestation of the fact that dislocations are not topologically stable excitations in glasses. The Burger's vector can be continuously decreased to zero without meeting any (topological) restrictions, although there may be energetic restrictions (barriers) inhibiting the creation or destruction of dislocations in this way. Disclinations, on the other hand, are quantized (as we saw in chapter 2) and any excitations of the curvature must be associated with 2π rotations. Such large rotations are unlikely to make a significant contribution to thermal fluctuations of η at low temperatures.

We can include the effect of fluctuations in η by introducing a random, thermal (Maxwellian) distribution of dislocations (torsion) as follows:

$$
\begin{aligned}
Z = & \int DT \int D\chi (\exp -\beta \int d^3\underline{x}[2\mu(\chi_{mn}(x)+\frac{\upsilon}{1-\upsilon}\delta_{mn}\chi_{pp}(\underline{x}))\nabla^4\chi_{mn}(\underline{x})]) \\
& (\exp -\beta\gamma\int d^3\underline{x}\, T_{mn}(\underline{x})T_{mn}(\underline{x}))(\delta(\eta^{Q}_{ij}(\underline{x})+\eta^{T}_{ij}(\underline{x})-\nabla^4\chi_{ij}(\underline{x}))
\end{aligned}
\tag{6.42}
$$

with $\eta^{T}_{ij} = -\frac{1}{2}(\epsilon_{ikl}\partial_k T_{lj} + \epsilon_{jkl}\partial_k T_{li})$ $\quad$ 6.43

Writing the δ function as a functional integral over an auxiliary field Λ, this becomes

$$
\begin{aligned}
Z = & \int D\Lambda \int DT \int D\chi \exp -\beta \int d^3\underline{x}(\chi_{mn}(\underline{x})M_{mnkl}\nabla^4\chi_{kl}(\underline{x})+\gamma T_{mn}(\underline{x})T_{mn}(\underline{x}) \\
& +\frac{i}{\beta}(\Lambda_{ij}(\underline{x})\eta^{Q}_{ij}(\underline{x})-\frac{\Lambda}{2}(\underline{x})(\epsilon_{ikl}\partial_k T_{lj}(\underline{x})+\epsilon_{jkl}\partial_k T_{li}(\underline{x}))-\Lambda_{ij}(\underline{x}) \\
& \nabla^4\chi_{ij}(\underline{x}))
\end{aligned}
\tag{6.44}
$$

with $M_{mnkl} = \mu(\delta_{mk}\delta_{nl} + \delta_{ml}\delta_{nk}) + \frac{2\mu\upsilon}{1-\upsilon}\delta_{mn}\delta_{kl}$ $\quad$ 6.45

In q space the partition function becomes:

$$
\begin{aligned}
Z = & \int D\Lambda(\underline{q})\int DT(\underline{q})\int D\chi(\underline{q})\exp-(2\Pi)^3\beta\int d^3\underline{q}[\chi_{mn}(\underline{q})M_{mnkl}\,\underline{q}^4\chi_{kl}(-\underline{q}) \\
& +\gamma T_{mn}(\underline{q})T_{mn}(-\underline{q})+\frac{i}{2\beta}(\Lambda_{ij}(\underline{q})\eta^{Q}_{ij}(-\underline{q})+\Lambda_{ij}(-\underline{q})\eta^{Q}_{ij}(\underline{q}))-\frac{i}{2\beta}(\Lambda_{ij}(\underline{q}) \\
& \qquad q^4\chi_{ij}(-\underline{q})+\Lambda_{ij}(-\underline{q})q^4\chi_{ij}(\underline{q})\Big) \\
& +\frac{1}{4\beta}(-\Lambda_{ij}(\underline{q})q_k(\epsilon_{ikl}T_{lj}(-\underline{q})+\epsilon_{jkl}T_{li}(-\underline{q}))+\Lambda_{ij}(-\underline{q})q_k \\
& \qquad (\epsilon_{ikl}T_{lj}(\underline{q})+\epsilon_{jkl}T_{li}(\underline{q}))]
\end{aligned}
\tag{6.46}
$$

The last factor can be rewritten as

$$-\frac{1}{4\beta}[(\Lambda_{ij}(\underline{q})+\Lambda_{ji}(\underline{q}))\varepsilon_{ikl}\, q_k T_{lj}(-\underline{q})\cdot(\Lambda_{ij}(-\underline{q})+\Lambda_{ji}(-\underline{q}))\varepsilon_{ikl}q_k$$
$$T_{j}(q)]$$

therefore the integral over T can be performed, leading to

$$Z = N_T\int D\Lambda(\underline{q})\int D\chi(\underline{q})\exp -(2\Pi)^3\beta\int d^3\underline{q}[\chi_{mn}(q)M_{mnkl}q^4\chi_{kl}(-\underline{q})$$
$$+\frac{i}{2\beta}(\Lambda_{ij}(\underline{q})\eta^Q_{ij}(-\underline{q})+\Lambda_{ij}(-\underline{q})\eta^Q_{ij}(\underline{q}))-\frac{i}{2\beta}(\Lambda_{ij}(\underline{q})q^4\chi_{ij}(-\underline{q})+\Lambda_{ij}$$
$$(-\underline{q})q^4\chi_{ij}(\underline{q}))+\frac{1}{16\beta^2\gamma}(\Lambda_{ij}(\underline{q})+\Lambda_{ji}(\underline{q}))\varepsilon_{ikl}\, q_k\varepsilon_{nml}\, q_m\cdot$$
$$(\Lambda_{jn}(-\underline{q})+\Lambda_{nj}(-\underline{q}))] \qquad 6.47$$

$$= N_T N_\chi \int D\Lambda(\underline{q})\exp -(2\Pi)^3\beta\int d^3\underline{q}[\frac{1}{4\beta^2}\Lambda_{ij}(\underline{q})q^4(\frac{1}{q^4}M^{-1}_{ijkl})q^4$$
$$\Lambda_{kl}(-\underline{q})+\frac{1}{16\beta^2\gamma}\Lambda_{ij}(\underline{q})(\varepsilon_{ipr}\varepsilon_{kmr}\delta_{jl}+\varepsilon_{ipr}\varepsilon_{lmr}\delta_{kj}+\varepsilon_{jpr}$$
$$\varepsilon_{kmr}\delta_{jl}+\varepsilon_{jpr}\varepsilon_{lmr}\delta_{ki})q_p q_m\Lambda_{kl}(-\underline{q})+\frac{i}{2\beta}(\Lambda_{ij}(\underline{q})\eta^Q_{ij}(-\underline{q})$$
$$+\Lambda_{ij}(-q)\eta^Q_{ij}(q))] \qquad 6.48$$

$$= N_T N_\chi\int D\Lambda(q)\exp-(2\Pi)^3\beta\int d^3q[\frac{1}{4\beta^2}\Lambda_{ij}(\underline{q})P_{ijkl}(\underline{q})\Lambda_{kl}(-\underline{q})$$
$$+\frac{i}{2\beta}(\Lambda_{ij}(\underline{q})\eta^Q_{ij}(-\underline{q})+\Lambda_{ij}(-\underline{q})\eta^Q_{ij}(\underline{q}))] \qquad 6.49$$

$$= N_T N_\chi N_\Lambda\exp -(2\Pi)^3\beta\int d^3\underline{q}\ \eta^Q_{ij}(\underline{q})P^{-1}_{ijkl}(\underline{q})\eta^Q_{kl}(-\underline{q}) \qquad 6.50$$

with $P_{ijkl} = q^4 M^{-1}_{ijkl}+\frac{1}{4\gamma}q_p q_m(\varepsilon_{ipr}\varepsilon_{kmr}\delta_{jl}+\varepsilon_{ipr}\varepsilon_{lmr}\delta_{kj}$
$$+\varepsilon_{jpr}\varepsilon_{kmr}\delta_{il}+\varepsilon_{jpr}\varepsilon_{lmr}\delta_{ki}) \qquad 6.51$$

Using the identity $\varepsilon_{ijk}\varepsilon_{lmk}=\delta_{il}\delta_{mj}-\delta_{im}\delta_{jl}$

this becomes

$$P_{ijkl} = q^4 M^{-1}_{ijkl}+\frac{1}{4\gamma}(2\delta_{ik}\delta_{jl}\, q^2+2\delta_{il}\,\delta_{jk}q^2-q_i q_k\delta_{lj}$$
$$-q_i q_l\,\delta_{jk}-q_j q_k\,\delta_{il}-q_j q_l\,\delta_{ik}) \qquad 6.52$$

But $M_{ijkl} = \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \frac{2\mu\upsilon}{1-\upsilon}\,\delta_{ij}\delta_{kl}$

Let $M^{-1}_{klpq} = A\,(\delta_{kp}\delta_{lq} + \delta_{kq}\delta_{lp}) + B\,\delta_{kl}\delta_{pq}$ 6.53

therefore $M_{ijkl}\,M^{-1}_{klpq} = \delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}$ 6.54

hence $A = \frac{1}{2\mu}$ and $B\,(2\mu + \frac{6\mu\upsilon}{1-\upsilon}) = \frac{-2\upsilon}{1-\upsilon}$ 6.55

or $B = \frac{-\upsilon}{\mu(1+2\upsilon)}$

Now $P_{ijkl} = X(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + Y\,\delta_{ij}\delta_{kl}$

$+ Z\,(q_iq_k\,{}_{jl} + q_iq_l\delta_{jk} + q_jq_k\delta_{il} + q_jq_l\delta_{ik})$ 6.56

with $X = \frac{q^4}{2\mu} + \frac{q^2}{2\gamma}$ 6.57

$Y = -\frac{\upsilon q^4}{\mu(1+2\upsilon)}$ 6.58

$Z = -\frac{1}{4\gamma}$ 6.59

For the inverse of this tensor, defined by

$P_{ijkl}\,P^{-1}_{klmn} \doteqdot (\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})$ 6.60

we try $P^{-1}_{klmn} = D(\delta_{km}\delta_{ln} + \delta_{kn}\delta_{lm}) + E\delta_{kl}\delta_{mn}$

$+F(q_kq_m\delta_{ln} + q_kq_n\delta_{lm} + q_lq_m\,\delta_{kn} + q_lq_n\,\delta_{km})$

$+G(q_kq_lq_mq_n) + H\,q_kq_l\,\delta_{mn} + I\,q_mq_n\,\delta_{kl}$

6.61

Thus we have 6 equations for the 6 unknowns:

$2XD = 1$ 6.62

$2XE + 2YD + 3YE + YHq^2 = 0$ 6.63

$2XF + 2ZD + 2ZFq^2 = 0$ 6.64

$2XG + 8ZF + 4ZGq^2 + 4ZI = 0$ 6.65

$4YF + YG\,q^2 + 2XI + 3\,YI = 0$ 6.66

$4ZE + 2XH + 4ZHq^2 = 0$ 6.67

From 6.62 $$D = \frac{1}{2X} \tag{6.68}$$

equation 6.67 gives $$H = \frac{-2ZE}{X+2Zq^2} \tag{6.69}$$

and substituting 6.69 into 6.63 leads to

$$E = \frac{-Y(X+2Zq^2)}{X[-2ZYq^2+(2X+3Y)(X+2Zq^2)]} \tag{6.70}$$

and $$H = \frac{2ZY}{X[-2ZYq^2+(2X+3Y)(X+2Zq^2)]} \tag{6.71}$$

From 6.64 $$F = \frac{Z}{2X(X+Zq^2)} \tag{6.72}$$

and 6.65 leads to

$$I = \frac{-(4YF+YGq^2)}{2X+3Y} = \frac{-1}{4Z}(4ZGq^2+8ZF+2XG) \tag{6.73}$$

therefore $$G = \frac{16YFZ-(2X+3Y)8ZF}{(2X+3Y)(4Zq^2+2X)-4ZYq^2} \tag{6.74}$$

In fact only the constants D and E are relevant for the interaction energy (equation 6.50) because the continuity equation for η^Q (equation 6.44) in q space is

$$q_i \eta^Q_{ij} = q_j \eta^Q_{ij} = 0 \tag{6.75}$$

therefore the terms involving F, G, H and I in equation 6.50 will be identically zero.

Substituting 6.57 into 6.68 we have

$$D = \left(\frac{q^4}{\mu} + \frac{q^2}{\gamma}\right)^{-1} \tag{6.76}$$

and similarly $$E = \frac{2\upsilon\gamma^2\mu}{(1-\upsilon)(q^2\gamma+\mu)(q^2\gamma+\mu(1+\frac{2\upsilon}{1-\upsilon}))} \tag{6.77}$$

Now the free energy $F = -\frac{1}{\beta} \ln Z$, with Z given by equation 6.50, becomes

$$F = \frac{-1}{\beta}\left[\ln N_T + \ln N_\chi + \ln N_\Lambda\right] + F_{int} \qquad 6.78$$

and $$F_{int} = (2\Pi)^3 \int d^3\underline{q}\; \eta^Q_{ij}(\underline{q})\; P^{-1}_{ijkl}\; \eta^Q_{kl}(-\underline{q}) \qquad 6.79$$

is the interaction energy of the intrinsic defects, in the presence of fluctuations. Returning to the real space representation:

$$F_{int} = \frac{1}{(2\Pi)^3} \int d^3\underline{x} \int d^3\underline{x}^1 \eta^Q_{ij}(\underline{x}) \int d^3q\; e^{-i\underline{q}(\underline{x}-\underline{x}^1)} P^{-1}_{ijkl}(\underline{q})\eta^Q_{kl}(\underline{x}) \qquad 6.80$$

where $$\int d^3\underline{q}\;\; e^{i\underline{q}(\underline{x}-\underline{x}^1)}\; P^{-1}_{ijkl}(q) = D\,(\underline{x}-\underline{x}^1)(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) + E(\underline{x}-\underline{x}^1)\;\delta_{ij}\delta_{kl} \qquad 6.90$$

and $$D(\underline{y}) = \int d^3\underline{q}\;\; e^{-i\underline{q}\cdot\underline{y}}\; D(\underline{q}) \qquad 6.91$$

$$= \int d^3\underline{q}\; \frac{\mu}{q^2(q^2+\frac{\mu}{\gamma})}\;\; e^{-iq\underline{y}} \qquad 6.92$$

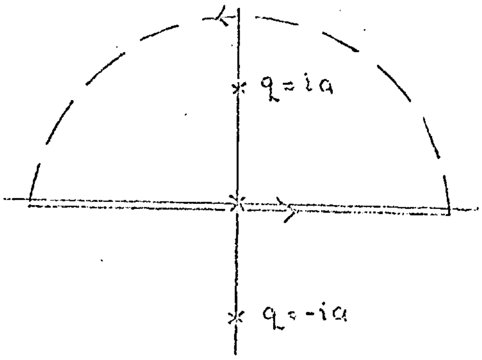
$$= 2\Pi\mu \int_0^\infty q^2 dq \int_{+1}^{+1} d\lambda\; \frac{e^{-iqy\lambda}}{q^2(q^2+\frac{\mu}{\gamma})} \qquad (\lambda = \mathrm{Cos}\,\theta) \qquad 6.93$$

$$= \frac{-2\Pi\mu}{iy} \int_0^\infty dq\; \frac{e^{-qyi}-e^{iqy}}{q(q^2+\frac{\mu}{\gamma})} \qquad 6.94$$

$$= +\frac{2\Pi\mu}{iy} \int_{-\infty}^{+\infty} dq\; \frac{e^{iqy}}{q(q^2+a^2)} \qquad (a^2 = \frac{\mu}{\gamma}) \qquad 6.95$$

$$= \frac{2\Pi\mu}{iy} \int_{-\infty}^{+\infty} dq\; \frac{e^{iqy}}{a^2}\; \left(\frac{1}{q} - \frac{1}{2(q+ia)} - \frac{1}{2(q-ia)}\right)) \quad 6.96$$

Closing the contour at $q = +i\infty$ then contour at ∞ does not contribute and we pick up 2 poles at $q = ia$ and $q = 0$. Thus



$$D(v) = \frac{4\Pi^2\gamma}{y}\left(\tfrac{1}{2}-\tfrac{1}{2}e^{-ay}\right) \qquad . \; 6.97$$

or $$D(y) = \frac{2\Pi^2\gamma}{y}\left(1-e^{-(\frac{\mu}{\gamma})^{\frac{1}{2}}y}\right) \qquad 6.98$$

Similarly

$$E(y) = \frac{2\upsilon\mu}{1-\upsilon} \int e^{-iq\cdot y} \frac{d^3q}{(q^2+\frac{\mu}{\gamma})(q^2+\frac{\mu}{\gamma}(1+\frac{2\upsilon}{1-\upsilon}))} \qquad 6.99$$

$$= \frac{4\Pi\upsilon\mu}{i(1-\upsilon)y} \int_{-\infty}^{+\infty} \frac{dq\; q\; e^{iqy}}{(q^2+a^2)(q^2+a'^2)} \qquad 6.100$$

with $a^2 = \frac{\mu}{\gamma}$

$a'^2 = \frac{\mu}{\gamma}(1+\frac{2\upsilon}{1-\upsilon})$

or $E(y) = \frac{2\Pi^2\gamma}{y} \left(e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}y} - e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}(1+\frac{2\upsilon}{1-\upsilon})^{\frac{1}{2}}y}\right)$

Therefore

$$F_{int} = \frac{\gamma}{4\Pi} \int d^3x \int d^3\underline{x}' \; \eta^{Q}_{ij}(\underline{x}) \frac{1}{|\underline{x}-\underline{x}'|} \Big[\Big(1-e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}'|}\Big)$$

$$(\delta_{ik}\delta_{jl} + \delta_{il}\,\delta_{jk}) + \Big(e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}'|} -$$

$$e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}(1+\frac{2\upsilon}{1-\upsilon})^{\frac{1}{2}}|\underline{x}-\underline{x}'|}\Big)\delta_{ij}\delta_{kl}\Big]\eta^{Q}_{kl}(\underline{x}') \qquad 6.102$$

If $\gamma \to 0$ (the width of the distribution tends to infinity) $F_{int} \to 0$ therefore the strain field of the intrinsic defects is completely screened by the fluctuations and they do not interact. On the other hand if $\gamma \to \infty$ we can expand the exponential in terms of the small parameter $\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}$:

$$\lim_{\gamma\to\infty} F_{int} = \lim_{\gamma\to\infty} \frac{\gamma}{4\Pi} \int d^3\underline{x} \int d^3\underline{x}' \eta^{Q}_{ij}(\underline{x}) \Big[\Big(\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}} - \frac{1}{2}\left(\frac{\mu}{\gamma}\right)|\underline{x}-\underline{x}'|\Big)$$

$$(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \Big(\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}\Big(\Big(1+\frac{2\upsilon}{1-\upsilon}\Big)^{\frac{1}{2}}-1\Big) - \frac{2\mu\upsilon}{2\gamma(1-\upsilon)}|\underline{x}-\underline{x}'|\Big)$$

$$\delta_{ij}\delta_{kl}\Big]\eta^{Q}_{kl} \qquad 6.103$$

$$= \lim_{\gamma\to\infty} \frac{\gamma\mu}{2\Pi} \int d^3\underline{x} \int d^3\underline{x}' (\eta^Q_{ij}(\underline{x}) + \tfrac{1}{2}\delta_{ij}\eta^Q_{kk}(\underline{x})((1+\frac{2\upsilon}{1-\upsilon})^{\frac{1}{2}}-1)$$

$$\eta^Q_{ij}(\underline{x}')-\frac{\mu}{4\Pi} \int d^3\underline{x} \int d^3\underline{x}' (\eta^Q_{ij}(\underline{x})+\frac{\upsilon}{1-\upsilon}\eta^Q_{kk}(\underline{x})\delta_{ij})|\underline{x}-\underline{x}'|\eta^Q_{ij}(\underline{x}') \qquad 6.104$$

and, apart from an (infinite) constant the interaction energy reduces to that without fluctuations (equation 6.43). The screening is inoperative in this limit.

The normalization constants (N_T, N_ℓ, N_Λ) in the free energy (6.78) are given by the following expressions:

$$N_T = \int DT(q) \exp - (2\Pi)^3 \beta\gamma \int d^3\underline{q}\ T_{mn}(\underline{q})\ T_{mn}(-\underline{q}) \qquad 6.105$$

$$= \exp -\tfrac{1}{2} \int d^3\underline{q}\ \ln\ \beta\gamma \qquad 6.106$$

This is, in fact, the normalization factor for the Maxwellian distribution. It should be set equal to unity if the total probability (area under the distribution) is normalized to 1.

Similarly

$$N_\ell = \int D\ell(\underline{q}))\exp -\beta \int d^3\underline{q}\ \ell_{mn}(\underline{q}) M_{mnkl} q^4 \ell_{kl}(-\underline{q}) \qquad 6.107$$

$$= \exp - \tfrac{1}{2} \int d^3\underline{q}\ \ln(\beta q^4\ \mathrm{Det}\ M) \qquad 6.108$$

$$= \exp - \tfrac{1}{2} (\ln\beta + \mathrm{Tr}\ \ln M)\ 4\pi q_{max} + \int d^3\underline{q}\ \ln q^4 \qquad 6.109$$

$$= \exp - 2\Pi\ [(\ln\beta + 3\ln(2\mu) + 3\ \ln(2\mu + \frac{2\mu\upsilon}{1-\upsilon}))q_{max}$$

$$+ \frac{4}{3} q^3_{max}\ (\ln q_{max} - \tfrac{1}{3})] \qquad 6.110$$

Here q_{max} is the natural cut off for q and is of the order of $\frac{1}{a}$ where a is the interatomic distance. A term of this form would also occur in a similar treatment for crystals (with zero quenched incompatibility) and has therefore no particular relevance to glasses.

The last normalization constant is given by:

$$N_{\Lambda} = \int D\Lambda(\underline{q}) \exp -\beta \int d^3\underline{q} \frac{1}{4\beta^2} \Lambda_{ij}(\underline{q}) P_{ijkl} \Lambda_{kl}(-\underline{q}) \qquad 6.111$$

$$= \exp - \tfrac{1}{2} \int d^3\underline{q} \quad \ln \frac{1}{4\beta} \text{ Det } P \qquad 6.112$$

$$= \exp + 2\Pi \quad q_{max} \ln 4\beta - \int q^2 dq \quad \ln(\text{Det } P) \qquad 6.113$$

Within this description a glass differs from a crystalline continuum in two ways:

1) $\eta^Q = 0$ in a crystal whereas it is finite in a glass.

2) γ crystal >> γ glass because in a crystal there are topological barriers inhibiting the creation of dislocations. In other words, fluctuations in η will be much stronger in a glass than in a crystalline continuum.

Thus the free energy difference arises from the term $\frac{2\Pi}{\beta} \int q^2 dq \ln \text{Det } P$, where P is a function of γ, and from the interaction energy of the intrinsic defects (F_{int}) which is zero in a crystal but given by equation 6.102 in a glass. However from 6.56

$$P_{ijkl} = \left(\frac{q^4}{2\mu} + \frac{q^2}{2\gamma}\right)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{\upsilon q^4}{\mu(1+2\upsilon)}\delta_{ij}\delta_{kl}$$

$$-\frac{1}{4\gamma}(q_i q_k \delta_{jl} + q_i q_l \delta_{jk} + q_j q_k \delta_{il} + q_j q_l \delta_{ik})$$

$$= q^4 M^{-1}_{ijkl} + O\left(\frac{1}{\gamma}\right) \text{ for large } \gamma \qquad 6.114$$

Writing $\ln(\mathrm{Det}\,P) = \mathrm{Tr}\,\ln\left(q^4 M^{-1} + \frac{1}{\gamma} N + O\left(\frac{1}{\gamma^2}\right)\right)$ 6.115

where $N_{ijkl} = \frac{q^2}{\gamma}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$

$$-\tfrac{1}{4}(q_i q_k \delta_{jl} + q_i q_l \delta_{jk} + q_j q_k \delta_{il} + q_j q_l \delta_{ik})$$

6.116

then $\ln(\mathrm{Det}\,P) = \mathrm{Tr}\,\ln q^4 M^{-1}(\mathbb{1} + \frac{1}{\gamma} MNq^{-4})$ 6.117

$$= \mathrm{Tr}\left(\ln(q^4 M^{-1}) + \ln(\mathbb{1} + \frac{1}{\gamma} MNq^{-4})\right) \qquad 6.118$$

$$= \mathrm{Tr}\,\ln q^4 M^{-1} + \mathrm{Tr}\left(\frac{1}{\gamma} MNq^{-4} + O\left(\frac{1}{\gamma}\right)^2\right) \qquad 6.119$$

$$= \ln q^4 - \mathrm{Tr}\,\ln M + \frac{1}{\gamma}\mathrm{Tr}\,MNq^{-4} \qquad 6.120$$

The first two terms of this expression combine with similar terms in $\ln N_{\phi}$, therefore we are left with

$$F = \frac{2\Pi}{\beta\gamma} \frac{dq}{q^2} \mathrm{Tr}(M_{ijkl} N_{klmn}) \qquad 6.121$$

$$= \frac{2\Pi}{\gamma} kT \int \frac{dq}{q^2} \mathrm{Tr}\left(q^2(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})\mu + \frac{2q^2\mu\upsilon}{1-\upsilon}\delta_{ij}\delta_{mn}\right.$$

$$-\tfrac{1}{4}\mu(2q_i q_n \delta_{jm} + 2q_j q_m \delta_{in} + 2q_j q_n \delta_{im} + 2q_i q_m \delta_{jn})$$

$$\left.-\frac{2\mu\upsilon}{(1-\upsilon)}\delta_{ij} q_m q_n\right) \qquad 6.122$$

$$= \frac{2\Pi}{\gamma} kT \int \frac{dq}{q^2} \tfrac{1}{2}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm}) [q^2\mu(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})$$

$$+\frac{2q^2\mu\upsilon}{1-\upsilon} \delta_{ij}\delta_{mn} - \frac{\mu}{2} (q_iq_n\delta_{jm} + q_iq_m\delta_{jn} + q_jq_n\delta_{im}$$

$$+q_jq_m\delta_{in}) -\frac{2\mu\upsilon}{1-\upsilon} \delta_{ij} q_mq_n] \qquad 6.123$$

$$= \frac{2\Pi}{\gamma} kT \int_{o}^{q_{max}} \frac{dq}{q^2} \left(12q^2\mu + \frac{6q^2\mu\upsilon}{1-\upsilon} - 4\mu q^2 - \frac{2\mu\upsilon}{1-\upsilon}\right)$$

$$\text{or} \qquad F_\gamma = \frac{8\Pi}{\gamma} \mu\left(2 - \frac{\upsilon}{1-\upsilon}\right) q_{max} kT \qquad 6.124$$

Thus the effect of fluctuations is to increase the entropy by a factor which (when γ is large) is inversely proportional to γ.

6.4 The Two Level System

In any particular configuration the excitations in the incompatibility (η^T) are indistinguishable from the intrinsic incompatibility (η^Q) and the total internal energy is given by:

$$U = -\frac{1}{4\Pi} \int d^3\underline{x} \int d^3\underline{x}^1 (\eta^T_{ij}(\underline{x}) + \eta^Q_{ij}(\underline{x}))M_{ijkl} |\underline{x}-\underline{x}^1|$$

$$(\eta^Q_{kl}(\underline{x}^1) + \eta^T_{kl}(\underline{x}^1)) \qquad 6.125$$

The nature of the low energy excitations of η becomes apparent if we write the interaction energy in terms of an integral along the defect line, a procedure made possible by the continuity equations (6.44).

$$\partial_i \eta_{ij} = 0, \ \partial_j \eta_{ij} = 0$$

Consider a defect line confined to a "tube" of cross section area a^2 then the integral of η over an elementary closed (cylindrical) surface of this tube vanishes because $\int \partial_i \eta_{ij}\, dV = 0 = \int \eta_{ij}\, ds\, \hat{n}_i$ 6.127

therefore the contribution from the top of the cylinder cancels that from the bottom (assuming no field flows out the side) and

$$a^2 \eta_{ij}\, \hat{n}_i = \text{Constant along the tube}$$

$$\doteq b_j \qquad 6.128$$

or $\eta_{ij} = \frac{1}{a^2}\, \hat{n}_i\, b_i$ 6.129

Here $\hat{n}$ is the tangent vector of the line defect. A similar argument using the second continuity equation leads to $\eta_{ij} = \frac{1}{a^2}\, \hat{n}_j\, b_i$ 6.130

and the symmetry of the field is preserved by writing $\eta_{ij} = \frac{1}{2a^2}\, (\hat{n}_i b_j + \hat{n}_j b_i)$ 6.131

Using this we can transform the volume integral of η into a line integral:

$$\int d^3\underline{x}\ \eta_{ij} = \int d\ell \int ds\ \ \eta_{ij} \qquad 6.132$$

$$= \int d\ell\ \tfrac{1}{2}\ (\hat{n}_i b_j + \hat{n}_j b_i) \qquad 6.133$$

$$= \tfrac{1}{2}(\int d\ell i\ b_j + \int d\ell_j b_i) \qquad 6.134$$

Therefore the interaction energy between two such lines (A,B) becomes (from (6.43):

$$U^{AB} = \frac{-\mu}{4\Pi}\Big[\frac{bm^A bm^B}{2} \int d\ell^A_n \int d\ell^B_n\ \ |\underline{x}^A - \underline{x}^B|$$

$$+ \frac{bm^A bn^B}{2}\ \int d\ell^A_n \int d\ell^B_m\ \ |\underline{x}^A - \underline{x}^B| + \frac{\upsilon}{1-\upsilon}\ b^A_m b^B_n \int d\ell^B_m$$

$$\int d\ell^A_n)\ |\underline{x}^A - \underline{x}^B| \qquad 6.135$$

or writing $|\underline{x}^A - \underline{x}^B|$ as r^{AB} this becomes

$$U^{AB} = -\frac{\mu}{4\Pi}\Big[\frac{\underline{b}^A\underline{b}^B}{2} \int\int d\underline{\ell}^A.d\underline{\ell}^B\ r^{AB} + \tfrac{1}{2}\int\int \underline{b}^A.d\underline{\ell}^B\ \underline{b}^B.d\underline{\ell}^A$$

$$+ \frac{\upsilon}{1-\upsilon} \int\int \underline{b}^A.d\underline{\ell}^A\ \underline{b}^B.\ d\underline{\ell}^B\ \ r^{AB}\Big] \qquad 6.136$$

The self energy of a defect loop is obtained by replacing B by A in equation 6.136. The self energy of any (intrinsic) defect line is, therefore, unchanged by the reversal of the line direction ($d\underline{\ell} \rightarrow -\ d\underline{\ell}$). The interaction energy between this defect and the surrounding defects is changed by such a transformation, however in the particular case when the defect is surrounded by an isotropic distribution of defects, the total energy of the two configurations (with opposite line orientation) is the same. An anisotropy in the distribution of the defects surrounding a given defect will tend to split the energy of the two orientations. The process of reversing the direction of an intrinsic defect line is effected by an excitation of the type: $n^T_{ij}(\underline{x}) = -2n^Q_{ij}(\underline{x})$ along the line, or the excitation of a defect of the opposite orientation and twice the strength of the original one. The barrier associated with this excitation is energetic (rather than topological) and the magnitude depends on the detailed structure of the medium.

Thus glasses (like spin glasses) have a distribution of two level systems associated with the reversal of the orientation of intrinsic defect lines. The anisotropy in the distribution of the surrounding defects splits the energy of the two configurations, but a finite density of zero energy excitations (corresponding to the defects with isotropic surroundings) remains. Coupling between the two level system and phonons occurs via the strain field of the defects.

6.5 Topological Excitations

In chapter 2 we saw that disclinations, associated with 2 Π rotations, are topologically stable excitations in glasses. The continuum model provides a natural framework for the discussion of such defects, in terms to the triad of vectors which was introduced as the field. The curvature introduced by the intrinsic defects implies that this field is not a unique function of space as parallel transport around a closed path does not, necessarily, return it to the initial configuration. This field is not, therefore, identical to the matter field of chapter 3 (which must be single valued) but it is similar to the combination of the matter field and gauge field ($\tilde{c}$). A closed path in real space maps on to an open path in configuration space (the manifold of internal states). The open path does, however, represent a reference configuration and fixes the starting point (i) and finishing point (f) for any mapping of the real space contour on to the Manifold of internal states. The presence of a topologically stable defect within the real space contour is signalled by a path in configuration space which cannot be continuously deformed into the reference path (Fig. 6.2). In fact the intrinsic curvature is generally small therefore any path in configuration space which crosses the surface of the sphere once signals the presence of a topological line defect within the real space contour, and knowledge of the reference state (low energy configuration) is not required.

Disclinations are associated with a large curvature (Rij) concentrated on the core and therefore (from equation 6.43) they interact via a linear potential ($|\underline{x}-\underline{x}^1|$). The interaction will, however, be screened by dislocations and thus it becomes (equation 6.102).

$$Uint = \tfrac{1}{4}\int d^3\underline{x}\int d^3\underline{x}^1 (Rij(\underline{x})+Rji(\underline{x}))\frac{\gamma}{4\Pi|\underline{x}'-\underline{x}|}[(1-e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}^1|})$$

$$(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})+(e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}^1|}$$

$$-e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}\left(1+\frac{2\upsilon}{1+\upsilon}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}^1|})\delta_{ij}\delta_{kl}](R_{ki}(\underline{x}^1)+R_{ik}(\underline{x}^1)) \tag{6.137}$$

$$= \int d^3\underline{x}\int d^3\underline{x}^1\ R_{ij}(\underline{x})\ \frac{\gamma}{4\Pi|\underline{x}-\underline{x}^1|}[(1-e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}^1|})(\delta_{ik}\delta_{jl}$$

$$+\delta_{il}\delta_{jk})+(e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}|\underline{x}-x^1|}-e^{-\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}\left(1+\frac{2\upsilon}{1-\upsilon}\right)^{\frac{1}{2}}|\underline{x}-\underline{x}^1|})$$

$$\delta_{ij}\delta_{kl}]\ R_{kl}(\underline{x}^1) \tag{6.138}$$

At distances ($|\underline{x}-\underline{x}^1|$) greater than $\left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}$ the exponential terms in the above expression can be neglected and the interaction potential $V_{ijkl}(\underline{x},\underline{x}^1)$ defined by

$$Uint = \int d^3\underline{x}\int d^3\underline{x}^1 R_{ij}(\underline{x})\ V_{ijkl}(\underline{x},\underline{x}^1)\ R_{kl}(\underline{x}^1) \tag{6.139}$$

becomes

$$V_{ijkl}(\underline{x},\underline{x}^1) = \frac{\gamma}{4\Pi|\underline{x}-\underline{x}^1|}\quad(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) \tag{6.140}$$

$$\text{for}\quad |\underline{x}-\underline{x}^1| > \left(\frac{\mu}{\gamma}\right)^{\frac{1}{2}}$$

The length $\left(\frac{\gamma}{\mu}\right)^{\frac{1}{2}}$ is a measure of the size of the "core" within which the distortion caused by the curvature is too large to be screened efficiently by dislocations.

Thus, in the presence of dislocations, disclinations interact (at least when the cores do not overlap) via a $\frac{1}{r}$ potential, therefore the total energy of a density ρ of disclinations (for $\rho^{-\frac{1}{2}} > \left(\frac{\gamma}{\mu}\right)^{\frac{1}{2}}$) has the form (equation 2.27) $E(\rho) = \frac{B\rho}{a} - \frac{A}{a}\rho \ln \rho a^2$ and they could be responsible for the Vogel-Fulcher law for the viscosity of supercooled liquids. The discussion of chapter 2 shows also that there is a finite density of disclination excitations in thermal equilibrium above the Fulcher or Kauzmann temperature (To). Disclinations are not observed in crystals because the topological stability of dislocations means that they are not freely available to screen the distortion field of disclinations. The properties of disclinations in two dimensional crystals have been discussed by Halperin and Nelson (1979) who showed that they may be responsible for an interesting intermediate phase (the hexatic phase) between liquid and quasi-crystalline order, yet to be identified experimentally.

There, as above, the distortion field of the disclinations is screened by dislocations and they interact via a 1/r potential.

6.6 Conclusions

In this chapter we introduced a model of a glass which we considered from a macroscopic point of view to be an isotropic elastic continuum, with the glassiness included as quenched torsion and curvature. The torsion and curvature act as extended sources of stress and strain which increase the internal energy of the glass (with respect to the corresponding crystal) and can thus be regarded as the intrinsic defects of the model. The presence of intrinsic defects has the effect of introducing low energy excitations (in the form of reversals of defect line directions) which dominate the low temperature specific heat of glasses. Such two level systems couple to phonons through the strain field of the defect and will therefore affect the thermal conductivity and acoustic attenuation of the medium (chapter 1).

In addition to the low energy excitations there are topologically stable excitations (defects) which take the form of 2Π disclinations. The large strain field normally associated with (crystalline) disclinations is here screened by dislocations in such a way that the interaction potential is proportional to the inverse of the distance between the disclinations, at least when the cores do not overlap. Thus the properties (energy and entropy) of disclinations have a similar form to the line defects discussed in chapter 2, therefore their equilibrium density will follow a Vogel-Fulcher law.

The advantage of this continuum approach is that it should be applicable to any disordered medium which resembles an isotropic elastic continuum, with sources of internal stress, on a macroscopic scale. The nature of the bonding is, to a large extent, irrelevant although it will determine the elastic constants and the energy scale of the excitations and barriers. In a covalent glass the number of constraints (equation 5.5), and thus the density of intrinsic defects, increase with increasing co-ordination number, or in the language of Phillips (1979), the unsatisfied constraints in an overconstrained glass introduce intrinsic defects (in the form of quenched incompatibility) into the medium.

In general, however, the nature of the low energy excitations and the topological defects are common to all glasses, a necessary feature of any model which hopes to explain the occurrence of low temperature anomalies and the Vogel Fulcher law in such a wide variety of materials (metglass, covalent glass, polymers and oils).

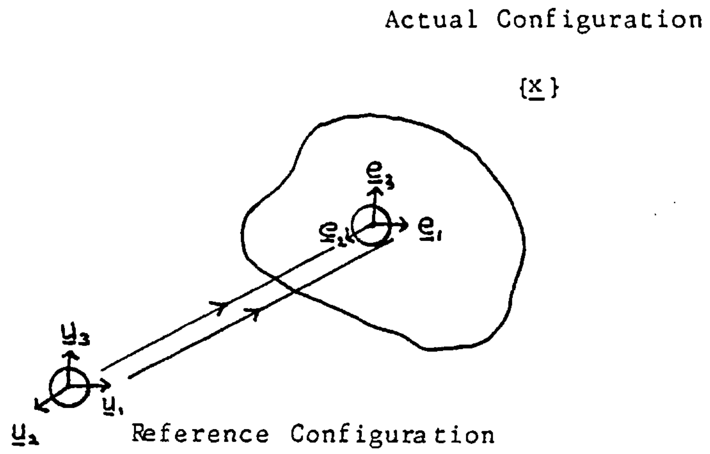


Figure 6.1

Schematic Representation of mapping between reference (relaxed) configuration and actual configuration.

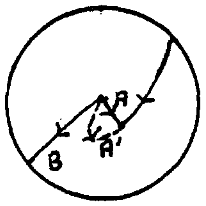


Figure 6.2

Manifold of internal states (SO(3)) is a solid sphere with opposite points on the surface identified.

The path A represents the reference path

A^1represents a trivial excitation which can be continuously deformed to the reference path.

B represents a nontrivial, topologically stable excitation of the system.

CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS

In this thesis we have discussed three continuous field theories of glasses which, on the face of it, look rather different. Table 7.1 summarizes the relevant properties of these models and from this it is evident that the general features are, in fact, very similar, although they vary considerably in detail. Each model has an underlying gauge invariance but the extent to which they are free to explore this invariance depends on the interpretation which we put on the gauge field. The phenomenological model of chapter 3 is invariant under the full rotation group and the gauge field is a free dynamical variable introduced solely to ensure this invariance, with no further physical significance. The Edward Anderson model of spin glass and the Keating model for covalent glass are also invariant under local rotations, however physical transformations are restricted to a smaller group (Z_2 in spin glass and ESQ(2) in the Keating model). This restriction is irrelevant in practice as the gauge fields (the interactions) are effectively quenched during the formation of the glass and there is no remaining gauge invariance in the system at low temperatures. In each case we define a new field which is a combination of the phase gradient of the matter field and the gauge field. This (Gauge invariant) field is then considered to be the only relevant field of the problem. The gauge invariance of the continuum model of glasses originates in the equilibrium condition on the stress field ($\partial_i \sigma_{ij} = 0$) which is, in some respects, analogous to Maxwell's equation ($\partial_i B_i = 0$) of electromagnetism.

In each model constraints, related to the structure of the underlying discrete network, are imposed on the fields. In a spin glass the constraints are imposed by quenching the curvature of the field (at least to within a vortex excitation) in such a way that it is finite only on well defined lines of the medium, corresponding to frustration lines of the discrete network. Such lines act as sources of the field and contribute to the free energy through an interaction energy which (for x-y spin glass and Heisenberg spin glass at low temperatures) has the same form as the interaction energy of current loops.

In a similar way the curvature of the field in the phenomenological model (chapter 3) is quenched, with a finite value only on well defined lines of the medium. These lines correspond to the lines threading the odd numbered rings in the underlying discrete continuous random network model of covalent glass. They act as sources of distortion and increase the internal energy of the glass.

The discrete Keating Model of a Covalent glass has constraints on the bond vectors, corresponding to the condition that all rings of bonds must close. Here there are two classes of constraint, one is the condition that the last bond must end where the first starts and the second is the rotational compatibility between the first and last bond. They are called torsion and curvature by analogy with similar effects in crystals. Rings which do not close in the relaxed (cut) configuration are associated with a finite torsion and they act as sources of distortion in the network.

The continuum model of a glass is also associated with finite torsion and curvature in the "ground state", originating from the internal stresses induced by ring closure constraints (torsion and curvature) of the underlying discrete network. From a macroscopic point of view, a glass is indistinguishable from a continuum representation of a crystal with dislocations and disclinations except that here the defects cannot be eliminated by relaxation. Disclinations are rare in crystals because of their large elastic energy but in a glass this is screened by dislocations which are not topological defects and can therefore be excited freely.

Thus, in each model the constraints take the form of extended sources of distortion and introduce energy density fluctuations into the medium. In some respects they resemble defects in ordered media and can therefore be regarded as intrinsic defects in glasses, however, unlike their crystalline counterparts, they cannot be removed by persistent relaxation and they are present even in "perfect" glasses.

Each of the continuum field theories discussed in this thesis introduces a specific model for the two level system, associated with the intrinsic defects. In the phenomenological model the two (equal energy) configurations are related by a nontrivial gauge transformation, effected by the excitation of a vortex of the matter field (and the gauge field) on an intrinsic defect loop. For such a process it is necessary that the gauge field is a free, independent variable, which is not the case in the spin glass model where the gauge field is related to quenched physical parameters (the interactions) and the only relevant field is the combination of the gauge field and matter field. In a spin glass the two configurations are, again, related by a topological (vortex like) excitation of the spin field, centred on an intrinsic defect loop. The energy of the two configurations, in the case of an isolated loop, are equal but the presence of other defects has the effect of splitting the levels. In a similar way the orientation of an intrinsic defect in the continuum model of a glass (chapter 6) can be reversed by the excitation of a dislocation loop. The dislocation is not a topological excitation in a glass therefore the barrier separating the two configurations is energetic, rather than topological, and again they have the same energy for an isolated loop, or a loop surrounded by an isotropic distribution of defects. Coupling between the two level system and phonons occurs via the strain field of the defect loop and this would explain the anomalous phonon scattering observed in low temperature acoustic and thermal conductivity experiments.

In addition to the tunnelling modes, which affect the low temperature thermal and acoustic properties, there are topological excitations, present in thermal equilibrium, only at high temperatures (above To as discussed in chapter 2). Such excitations are, in each of the models, associated with a rotation of the order parameter by 2Π around a singular line. The lines move freely in the medium and their topological stability implies that they must satisfy a conservation law and cannot, therefore, decay spontaneously.

In the gauge invariant model of chapter 3 such defects are associated with singularities of the matter field. This induces a curvature of the gauge field which tends to screen the distortion field ($\tilde{C}$) of the singularity. In the semidilute regime (when the average distance between defects is less than the self screening length of the singularity) such defects interact via a 1/r potential.

In a spin glass the excitations are vortices of the spin field which rotates by 2Π, with respect to the ground state configuration, around the singular line. In a Heisenberg ferromagnet such vortices are not topologically stable but the noncollinear spins of a spin glass has the effect of stabilizing line defects with 2Π rotations. In an x-y model the vortices interact via a 1/r potential but in a Heisenberg model, at the temperatures at which the number of vortices is significant, the nonlinearity of this model is important and the interaction is more complicated.

As in a spin glass, the "order parameter" in the continuum model of a glass is defined with respect to a particular low energy configuration. Parallel transport of a triad of vectors around a closed contour in the reference (low energy) configuration may result in a finite rotation of the triad. Topological excitations are associated with additional 2 Π rotations. The strain field associated with this large rotation is screened by dislocations, which are not topologically stable and can therefore be created and decay spontaneously. The effect of such screening is to cause the strain field to decrease as the inverse of the distance from the line, therefore the disclinations interact via a 1/r potential, as they do in liquid crystals.

Thus topological excitations, and their interactions, are identical in all the models considered in this thesis. The argument of chapter 2 is quite general and relies solely on the topological stability of line defects. The high temperature (T> To) properties of glasses (their relaxation and the Kauzmann Paradox) can therefore be satisfactorily explained by a simple concept, valid in general.

Although the intrinsic defects appear reasonably similar in the various models considered, there are some apparent differences in the models of the two level system. In the phenomenological and spin glass models the transition between the two configurations is effected by the excitation of a topological defect, although in the first case it is a gauge transformation (therefore the two configurations always have equal energy) and in the second case it is not. In the continuum glass model it appears that the transition is effected by the excitation of a nontopological defect (a dislocation) and the barrier must be energetic (rather than topological). This has the effect (as in the spin glass case) of reversing the orientation of an intrinsic defect line. It has been known for some time that the concept of the two level system has universal validity in glasses and a direct, overriding influence on the low temperature properties. In this thesis we suggest specific models for the two level system which are a natural consequence of the universal features of glass (homogeneity or gauge invariance) and intrinsic defects) although it remains to be shown whether such models are unique.

TABLE 7.1

CHAPTER	3	4	5	6
Field Theory for:	All glasses	Spin Glass	Covalent glass (Discrete)	All atomic and molecular glasses
Hamiltonian	$\int d^3\underline{x}\ (\hat{D}_\mu\hat{\emptyset})^{ij}(\hat{D}_\mu\hat{\emptyset})^{ij} + U(\hat{\emptyset}) + \frac{1}{2}\hat{F}^{ij}_{\mu\upsilon}\hat{F}^{ij}_{\mu\upsilon}$ (3.9) $\int d^3\underline{x}\, g^2[\tilde{C}\mu,\Omega_0]^{ij}[\tilde{C}_\mu,\Omega_0]^{ij}+\frac{1}{2}\tilde{F}^{ij}_{\mu\upsilon}\tilde{F}^{ij}_{\mu\upsilon}$ (3.40)	$\frac{Jg^2}{a}\int d^3\underline{x}\ \tilde{A}^{ij}_\mu(\underline{x})\tilde{A}^{ij}_\mu(\underline{x})$ (4.17)	$ga^2\sum_{\langle bb^1\rangle}(\alpha(\mathrm{Tr}\ \underline{A}_{bb^1})^2 + (\beta\,\mathrm{Tr}(\underline{\underline{A}}_{bb^1}^{2}))$ (5.42)	$2\mu\int d^3\underline{x}\ (\chi_{ij}+\frac{\upsilon}{1-\upsilon}\chi_{kk}\delta_i)\nabla^4\chi_{ij}$
Origin of Hamiltonian	Phenomenological	Edwards Anderson Model $\sum_{\langle bb^1\rangle}\underline{S}_i J_{ij}\underline{S}_j$ (4.6)	Keating model $\sum\frac{\alpha}{a^2}\sum_\mu(\underline{x}_{\ell\mu}^{2}-a^2)^2 + \frac{\beta}{a^2}\sum_{\langle\mu\upsilon\rangle}(\underline{x}_{\ell\mu}\cdot\underline{x}_{\ell\upsilon}-a^2\mathrm{Cos}^2\theta)^2$ (5.1)	Elasticity Theory $\int d^3\underline{x}\,\sigma_{ij}E_{ij}$

TABLE 7.1 Continued

CHAPTER	3	4	5	6
Field Theory For:	All glasses	Spin glass	Covalent glass (Discrete)	All atomic and molecular glasses
Gauge Invariance	(3.9) is invariant under local rotations $\tilde{C}\mu$ is gauge invariant	4.17 is invariant under local rotations $\tilde{A}\mu$ is gauge invariant	5.42 is invariant under restricted bond rotations $\tilde{A}\mu = (\prod_{\beta<\alpha} J_\beta)\underline{\underline{A}}_\alpha (\prod_{\beta<\alpha} J_\beta)^{-1}$ is gauge invariant	6.41 is invariant under the local transformation $\surd_{ij} \rightarrow \gamma_{ij} + (\partial_i U_j + \partial_j U_i)$
Intrinsic Defects	Lines of finite curvature $\tilde{F}^{\mu\upsilon} = \partial\mu \tilde{C}\upsilon - \partial_\upsilon \tilde{C}\mu + g(\tilde{C}\mu \tilde{C}\upsilon - \tilde{G}_\upsilon \tilde{C}\mu)$	Lines of finite curvature $\tilde{F}\mu\upsilon$ (frustration lines)	Closure failure of rings of bonds in relaxed configuration	Finite Torsion T_{ij} and Curvature R_{ij}: Combine to form incompatibility $\eta_{ij} : \eta_{ij} = (\epsilon_{ipr} \partial p \bar{T}^{r}_{j} + R_{ij})$ sym $= \nabla^4 \surd_{ij}$

CHAPTER	3	4	5	6
Field Theory For:	All glasses	Spin glass	Covalent glass (discrete)	All atomic and molecular glasses
Continuity Equation for Defects	Bianchi Identity $\tilde{D}_\mu \tilde{F}^{\mu\upsilon} = 0$	Bianchi Identity $\tilde{D}_\mu \tilde{F}^{\mu\upsilon} = 0$		Torsion Identity $(Di+2T^{j}_{ji})T^{i}_{k}=-\varepsilon_{ilk}R^{il}$ Bianchi Identity $(Di+2T^{j}_{ji})R^{ik} = 0$ and $\partial_i \eta_{ij} = 0$
Two level System	Large gauge transformation centred on intrinsic defects (excitation of a matter field vortex)	Reversal of orientation of frustration line by vortex excitation.		Reversal of orientation of intrinsic defect by excitation of a dislocation loop.
Topological Excitations	Singularity of matter field screened by gauge field	Vortex excitation of spin field.		2Π disclination, screened by dislocation.

APPENDIX 1

Proof of Equation 6.23

The strain field Ejk, given by equation 6.21, is

$$Ejk = \tfrac{1}{2}\, gjk - g_{KL}\, M^{-1K}\, j\, M^{-1L}\, k$$

or, in the linear approximation ($gjk = \delta jk$; $g_{KL} = \delta_{KL}$),

$$Ejk = \tfrac{1}{2}[\delta_{jk} - \delta_{KL}\, M^{-1K}{}_j\, M^{-1L}{}_k] \tag{A.1}$$

therefore
$$\partial_i E_{jk} = -\tfrac{1}{2}[\delta_{KL}(\partial_i M^{-1K}{}_j) M^{-1L}{}_k + \delta_{KL}\, M^{-1K}{}_j (\partial_i M^{-1L}{}_k)] \tag{A.2}$$

$$= -\tfrac{1}{2}\delta_{KL}[(M^{-1K}{}_\ell\, M^\ell{}_J)(\partial_i M^{-1J}{}_j) M^{-1L}{}_k + M^{-1K}{}_j (M^{-1L}{}_\ell M^\ell{}_J)\partial_i M^{-1J}{}_k\,] \tag{A.3}$$

and, using equation 6.5, this becomes

$$\partial_i\, E_{jk} = -\tfrac{1}{2}\delta_{KL}[\Gamma^\ell_{ji}\, (M^{-1K}{}_\ell\, M^{-1L}{}_k) + \Gamma_{ki}(M^{-1K}{}_j M^{-1L}{}_\ell)] \tag{A.4}$$

$$= -\tfrac{1}{2}[\Gamma^\ell_{ji}(\delta_{\ell k} - 2E_{\ell k}) + \Gamma^\ell_{ki}(\delta_{j\ell} - 2E_{j\ell})] \tag{A.5}$$

Keeping only first order terms in and E, this becomes

$$\partial i E_{jk} = -\tfrac{1}{2}[\Gamma_{kji} + \Gamma_{jki}] \tag{A.6}$$

Now defining $E_{ijk} \doteq \tfrac{1}{2}(\partial_i E_{jk} + \partial_j E_{ik} - \partial_k E_{ij})$ $\quad$ A.7

then
$$E_{ijk} = \tfrac{1}{4}(-\Gamma_{kji} - \Gamma_{jki} - \Gamma_{kij} - \Gamma_{ikj} + \Gamma_{ijk} + \Gamma_{jik}) \tag{A.8}$$

$$= \tfrac{1}{2}(T_{jik} + T_{ijk} - T_{kji}) - \tfrac{1}{2}\Gamma_{kij} \tag{A.9}$$

or
$$\Gamma_{kij} = -2E_{ijk} + (T_{kij} + T_{ijk} - T_{jki}) \tag{A.10}$$

therefore
$$\Gamma_{kij} = \varepsilon_{kiq}\, \varepsilon_{nrq} \partial_n\, E_{rj} - \partial_j E_{ik} + \tfrac{1}{2}(\varepsilon_{ijp} T_{kp} + \varepsilon_{jkp}\, T_{ip} - \varepsilon_{kip}\, T_{jp}) \tag{A.11}$$

$$= -\partial_j E_{ik} + \varepsilon_{kiq}\, (\varepsilon_{nrq} \partial_n\, E_{rj} - \tfrac{1}{2} T_{jq}) + \tfrac{1}{2}\, \varepsilon_{ikq}\, \varepsilon_{nrq}\, \varepsilon_{njp}\, T_{rp} \tag{A.12}$$

$$= -\partial_j E_{ik} + \varepsilon_{kiq}\, (\varepsilon_{nrq} \partial_n\, E_{rj} - T_{jq} + \tfrac{1}{2}\, \delta_{jq} T_{pp}) \tag{A.13}$$

Now $R_{kijl} \sim \partial_j \Gamma_{kil} - \partial_l \Gamma_{kij}$ A.14

and $R_{st} = \frac{1}{4} \epsilon_{kis} \epsilon_{j\ell t} R_{kij\ell}$ A.15

$$= \tfrac{1}{2} \epsilon_{kis} \epsilon_{j\ell t} \partial_j \Gamma_{ki\ell} \qquad \text{A.16}$$

$$= \tfrac{1}{2} \epsilon_{kis} \epsilon_{j\ell t} \epsilon_{kiq} \partial_j (\epsilon_{nrq} \partial_n E_{r\ell} - T_{\ell q} + \tfrac{1}{2} \delta_{\ell q} T_{pp}) \qquad \text{A.17}$$

$$= \epsilon_{nrs} \epsilon_{j\ell t} \partial_j \partial_n E_{r\ell} - \epsilon_{j\ell t} \partial_j T_{\ell s} + \tfrac{1}{2} \epsilon_{jst} T_{pp} \qquad \text{A.18}$$

The symmetric part of this equation gives

$$\epsilon_{nrs} \epsilon_{j\ell t} \partial_j \partial_n E_{r\ell} = (R_{st} + \epsilon_{j\ell t} \partial_j T_{\ell s}) \text{ symmetric} \qquad \text{A.19}$$

or $\eta_{st} = - (R_{st} + \epsilon_{j\ell t} \partial_j T_{\ell s})$ symmetric A.20

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