Atomistic Simulations to Study Metallic Glasses: A Microscopic Investigation of Local Structural Excitations

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ATOMISTIC SIMULATIONS TO STUDY METALLIC GLASSES:
A MICROSCOPIC INVESTIGATION OF LOCAL STRUCTURAL EXCITATIONS

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

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Abstract

In this thesis, structural excitations of 50/50 model binary Lennard-Jones glass systems are investigated using the Activation Relaxation Technique nouveau (ARTn), which explores the potential energy landscape of a local minimum energy configuration by converging to a nearby saddle-point configuration. Performing ARTn results in a distribution of barrier energies that is single-peaked for well relaxed samples. The present work characterises such atomic-scale excitations in terms of their local structure and environment. Such structural excitations are referred to as local structural excitations (LSEs). It is found that, at zero applied stress, many of the events identified consist of chain-like excitations that can either be extended or ring-like in their geometry. The location and activation energy of these saddle-point structures are found to mainly correlate with the type of atom involved, and with spatial regions that have low shear moduli and are close to regions of excess free volume within the configuration. In terms of environment such correlations are, however, weak and more generally the identified LSEs are seen to exist throughout the model glass sample. The potential energy landscape of a model binary Lennard-Jones structural glass is also investigated as a function of applied external strain, in terms of how LSEs respond to the load. Using the ARTn and the nudged elastic band (NEB) method, the evolving structure and barrier energy of such LSEs are studied in detail. For the case of a tensile/compressive strain the LSE barrier energies generally decrease/increase, whereas under pure shear, a dominant broadening of the distribution is seen. It is found that how a particular LSE responds to an applied strain is very much controlled by its far-field internal stress signature prior to loading.
Zusammenfassung

Chapter 1

Introduction

1.1 Motivation

Metallic glasses have found widespread applications in different fields of engineering since their discovery in 1960. Their most important application in the 1970s and 1980s was in transformer cores and magnetic devices due to the soft-magnetic properties of some of the Fe-based metallic glasses [1]. However, their use as structural material is rather limited due to their low ductility and brittle nature of failure at the macroscopic scale. Despite this, scientific and technological interest in glasses has gained momentum in the last decade owing to their promise of superior mechanical properties. The glass alloys have high strength (4 GPa) and a high elastic limit (2%) which is significantly higher than that of their crystalline counterparts. However, specific challenges that need to be addressed to make the plastic properties of metallic glasses suitable for structural applications are, 1) a need for clear understanding of the exact deformation mechanism at the atomic scale that governs plasticity, and 2) control over its failure mechanism. The precise relationship between the atomistic mechanisms that occur at the microscopic length scale and the experimentally
observed formation of shear bands is yet to be fully understood. Shear bands are known to be the carriers of plasticity at macroscopic length scales. The brittle failure of metallic glasses is due to the formation of such highly localized shear bands, where the deformation energy is concentrated in a local volume. Understanding of shear-band formation, their arrest and control is therefore of paramount importance in understanding the failure of metallic glasses. It was the goal of this thesis project to study the underlying atomic-scale processes that collectively lead to such macroscopic plasticity. This effort has the longer term objective of linking the microscopic deformation behaviour of amorphous metals with the experimentally observed shear bands and their properties.

Computer simulations have significantly contributed to the field of amorphous materials and continue to play an important role in formulating glass theories. What makes simulations prominent is the absence of experimental devices to directly measure the atomic-scale plastic events in glasses, unlike the situation for crystalline materials, where dislocations are captured via electron microscopy [2]. Hence, it is pivotal to rely on modern computer models to develop theories of glass plasticity. In this thesis work, atomistic simulations of model glass systems were performed in order to study microscopic plastic deformation mechanisms in amorphous systems with the goal of drawing out their relevance with experiments on glasses that are carried out at larger length scales.

To solve the application-oriented engineering scale challenges of metallic glasses, it is important to formulate the relationship between its microscopic disorder and macroscopic material properties via which one can gain control over the structural properties of glasses. In order to do so, concrete steps need to be taken to first understand the types of microscopic deformation behaviour in glasses that collectively contribute towards global plasticity. In the last decade, investigators have attributed the responsible atomistic mechanism to the phenomenological concept of shear transfor-
ation zones (STZ) [3, 4]. However, the exact nature and properties of the STZs are yet to be fully explored and understood in the materials science community, and is a matter of intense debate at international conferences. How STZs operate individually and collectively to mediate plasticity as a function of stress and temperature needs to be investigated to gain thorough understanding of the thermal and mechanical response of metallic glasses. The STZ concept is inherently athermal in nature. Thus it describes a glass plasticity which is stress driven. However, there is evidence for thermally activated structural excitations in metallic glasses that mediate plasticity. In this regime, microscopic plastic events that mediate glass plasticity are activated by thermal fluctuations. Furthermore, there is a limited understanding of how STZs relate to the nomenclature established by the undercooled liquids community, where two relaxation mechanisms have been identified at the microscopic scale, classified as $\beta$- and $\alpha$-relaxations [5]. Finding answers to these questions and improving upon the current understanding of the fundamental physics of glass plasticity can lead to the enhancement of its mechanical properties, thereby paving a way for developing its enormous untapped potential as a structural material. This intention motivates this thesis.

1.2 Literature review

1.2.1 Experiment

a) Glass production

Metallic glasses can be produced under laboratory conditions by rapid cooling of molten glass-forming alloys. The first metallic glass $Au_{81}Si$ was reported by [6] in 1960. Even though this first amorphous structure produced was unstable in nature, X-ray diffraction studies indicated the characteristic behaviour of a glassy structure.
In this work and in some of the early laboratory-produced metallic glasses, the glass-formers had to be cooled at an extremely high cooling rate (of the order of \(10^6\) K/s) to avoid crystallization. To achieve such a cooling rate, heat had to be removed fast enough from the specimen which necessiated one dimension of the glass specimen to be very small. Therefore, the thickness of the early amorphous structures formed were of the order of a few tens of micrometers in geometries of wires or thin foils. Since then, the field of metallic glasses has further developed. A select alloy composition in combination with contemporary casting techniques such as copper mold casting results in a significant reduction of the cooling rate that still retains the amorphous structure. In the 1990s, glass alloys were produced that had a critical cooling rate (i.e., the cooling rate necessary to avoid crystallization) as low as 1 K/s with thicknesses of the order of a few centimeters. Metallic glasses with a thickness greater than one millimeter are commonly known as bulk metallic glasses (BMGs). The chronological development of novel metallic glass systems is reviewed, for example, in Ref. [7].

Production of bulk metallic glasses involves two kinds of technique a) solidification, and b) consolidation; see [7] and references therein. Solidification techniques include experimental methods such as:

- **Water-quenching:** Rapid cooling of a molten glass former can produce a metallic glass. A fast quench can prevent all forms of crystallization to induce disorder in the quench product. When water is used as a quenchant or the medium of the quench, the technique is termed as water-quenching. Usually, the role of a quenchant is to control the severity of the quench.

- **Copper-mold casting:** In this method, the prealloys are first melted and the molten glass formers are injected into a copper mold cavity of a desired shape and size. The solidification of the melt inside the cavity leads to formation of the glass sample with the required dimensions.

- **High-pressure die casting:** In this technique, molten metal is injected into the
die cavity with considerable pressure. The pressure is controlled until the melt solidifies which is ejected from the die after solidification.

- **Arc-melting**: This process is normally used for alloying purposes and to improve the quality of the product to obtain a desired mechanical homogeneity. Typically, the prealloys are melted via an electric arc to form the alloy melt. The melting is carried out several times to ensure a certain degree of homogeneity. The solidification rate can be controlled in this method while cooling the melt inside a crucible typically made of copper.

- **Suction casting**: This method involves sucking of the molten metal into a die cavity by taking advantage of the pressure differential between the melting chamber and the casting chamber. The die is in contact with a vacuum source, which when activated, causes the pressure differential.

- **Squeeze casting**: Squeeze casting is a method in which a metal melt is poured into the bottom part of a pre-heated die. As the melt solidifies, the die closes from the top in such a way that mechanical pressure is applied on the solidifying melt.

**b) Glass structure**

Long-range order is a property where structural units of the material repeat themselves. It is the absence of long-range order in the atomic arrangement of amorphous solids that distinguishes them from their crystalline counterparts. However, amorphous metals such as glasses possess short-range order (SRO), where structural patterns repeat in a length scale that is limited to the nearest neighbouring atoms. Characteristic defining features of the SRO in a particular system are the nearest-neighbour distance and the coordination number. How the short range order units arrange themselves defines the medium-range order (MRO) in glasses.
Since the discovery of metallic glasses, questions have been asked pertaining to the role its atomic structure plays in determining its glass-forming ability (GFA). Several structural models have been proposed but only with partial success. Due to the structural similarities between glasses and liquids, in the early 1960s, the metallic glass (MG) community adopted the dense random packing (DRP) model, which was primarily designed for monoatomic liquids [8]. This was not appropriate for MGs, because MGs are always known to have more than one atomic species in their composition. In the interstitial voids of the DRP model, it was endeavoured to put another atom (of a different size) to comply with MGs [9]. However, this approach was unsuccessful because the voids in the DRP model were much smaller when compared with the size ratios of atomic species in MGs. In the late 1970s, the stereo-chemically defined (SCD) model was proposed by Gaskell [10], and was an important milestone in explaining the atomic structure of MGs.

The efficient cluster packing (ECP) model was proposed by Miracle [11] to explain the atomic structure of MGs. The elementary structural units in this model are fcc or hcp clusters which are centered around the solute atom. A schematic depiction of
the model is shown in Fig.1.1, where \( \alpha \) atoms are the primary solute atoms which are at the centre of the cluster that comprises of the solvent atoms \( \Omega \), and secondary and tertiary solute atoms \( \beta \) and \( \gamma \), respectively, which fill up the interstitial voids. Efficient packing is the aim; hence the use of hcp and fcc units, which are known to fill up space efficiently.

In this model solvent atoms are placed randomly and solute atoms are positioned such that they satisfy the medium-range order (MRO) observed in MGs. This model suggests that there can be no more than three solute atom types contrary to the conventional knowledge that MGs can contain any number of solute atom types. The ECP model can predict the number of solute atoms which are in the range of MRO, thereby devising a pathway for predicting MG composition. The atomic structure understanding of GFA is a significant step towards developing a proper method to create MGs out of a vast compositional space. In the past, MGs have often been produced via a trial-and-error method [12]. Proper understanding of the atomic structure of MGs and its correlation with GFA will therefore set a guideline for the discovery of new bulk metallic glasses.

In recent works [13, 14], varying degrees of SRO in metallic glasses were discussed. In these works, the authors suggest that by manipulating the population of the different types of SRO seen in MGs, its properties can be controlled. In [14], the author observed that MGs have been viewed in literature as composed of polyhedra that are topologically and chemically favoured locally. For example, one of the most favoured coordination polyhedra is a regular icosahedron with 20 faces and 12 vertices, with a coordination number of 12. The favoured SROs correlate with several properties of glasses. The evolution of the population of SRO in a glassy system is related to its stability and is also believed to be closely linked to its potential energy. In a recent work [15, 16], the icosahedral SRO in MGs has been investigated in a computer-modelled CuZr glass. Among the polyhedral SRO discussed in [17], a high percentage of icosa-
hedral models was found. Different types of icosahedral SRO are generally found in the atomic structure of MGs. In [16], MD simulations were carried out on a model CuZr glass to simulate the “isothermal holding” process. It was found that as the percentage of icosahedra in the simulated glass sample increases, the system evolves towards another phase, called the Laves phase. This phase leads to an increase in the strength of the MG and a reduction in plasticity.

c) Mechanical properties

The mechanical properties of BMGs can be summarized based on the experimentally derived deformation map shown in the review article of Ref. [18]. In Fig. 1.2a, the normalized shear stress is plotted against the dimensionless temperature \((T/T_g)\), where \(T\) is the true temperature and \(T_g\) is the glass transition temperature. The deformation behaviour portrayed in this figure clearly shows three distinct deformation regimes as a function of shear stress and temperature. The first is an elastic regime which is observed at temperatures well below the glass transition temperature and at low enough stresses. In this regime, the flow is negligible. However, flow completely ceases only at extremely low temperatures. At temperatures around \(T_g\), and at low stresses, homogeneous flow is observed in glasses, a regime coloured in orange and yellow in Fig. 1.2a. In the homogeneous deformation regime, there are two sub-regimes, one where the material experiences Newtonian flow (at low stresses) and another sub-regime where non-Newtonian behaviour is seen. At higher stresses deformation is rather inhomogeneous for any given temperature. In this regime where shear is localized, the inhomogeneity usually takes the form of shear-band formation under compression [19, 20, 21, 22]. Under tension the material can fail via brittle-like fracture. In Fig. 1.2b, the rate of shear strain is plotted against dimensionless temperature \((T/T_g)\). The deformation can be broadly classified as homogeneous and inhomogeneous in nature. At low strain rate and high temperatures homogeneous flow
Homogeneous deformation

- Uniform plastic strain throughout the sample.
- Occurs at high temperature.
- Occurs at low strain rate.
- Flow can be Newtonian or non-Newtonian.
- There is no flow serration.
- Strong strain-rate effect.

Inhomogeneous deformation

- High plastic strain or strain-rate in a local region.
- Occurs at low temperature.
- Occurs at high strain rate.
- Localized in nature.
- Varying degrees of flow serration are seen as a function of increasing strain rate.
- Weak strain-rate effect.

Table 1.1: A comparison between homogeneous and inhomogeneous deformation in amorphous systems.

is noticed in glasses, which can be sub-divided into Newtonian and non-Newtonian flow depending on stress levels. The two sub-regimes are coloured in yellow and orange, respectively, in the same spirit as in Fig. 1.2a. At high strain rates and low temperatures the flow is inhomogeneous (coloured in blue). Varying degrees of flow serration in the inhomogeneous deformation regime are depicted which range from strongly serrated flow at relatively low strain rate to moderate and negligible flow serration at higher strain rates. Table 1.1 compiles the discussed features of homogeneous and inhomogeneous deformation in metallic glasses.
Figure 1.2: Homogeneous and inhomogeneous deformation (taken from ref. [18]).
1.2.2 Theory

a) Microscopic models

Unlike crystals, which contain well-defined defects such as dislocations, there exists no such defined microscopic process in glasses. Phenomenological theory and simulations have therefore played a central role in understanding plasticity of BMGs. In the pioneering work of Spaepen [23], a free volume model was proposed as the atomistic mechanism behind plastic flow in metallic glasses. In this model, single atoms migrate into regions of free volume. The underlying assumption of the Spaepen model is that the collective effect of such atomic jumps results in macroscopic flow which can be homogeneous or inhomogeneous in nature. In order to understand this model, a diagram depicting one atomic jump is shown in Fig. 1.3. In this diagram, one atom which is surrounded by neighbouring atoms migrates into a vacancy adjacent to it which is of the order of an atomic size. In order for this jump to occur, an activation energy is required which can be denoted by $\Delta G$. This barrier hopping is illustrated in the atomic distance vs energy plot in fig. 1.3. Once this barrier is overcome, the atom lands in a relatively stable region in the energy landscape which is different from the initial stable minimum. If there is no applied stress, the atom is energized via thermal fluctuations in order to cross the barrier. There is equal likelihood that the atom can migrate back to its original position via thermal fluctuations. Such back and forth motion of an atom near a region of free volume (whose dimensions are of the order of an atomic size or greater) leads to no net transport. However, if there is an applied shear stress on the surrounding atomic structure, the model suggests that the atomic jump is more likely to occur in the direction of the applied stress and jumping back to its original position is less probable due to the shear acting against the reverse motion. Such an assymmetrical atomic jump is the fundamental step towards global plastic flow in metallic glasses.

Spaepen constructed the governing flow equation based on his free volume model.
Figure 1.3: Free volume model by Spaepen, taken from ref. [23]

His flow equation is given by:

\[
\frac{\partial \gamma}{\partial t} = \Delta f \exp(-\gamma v^* v_f) 2\nu \sinh(-\frac{\tau \Omega}{2k_B T}) \exp(-\frac{\Delta G}{k_B T}),
\]

(1.1)

where \(\Delta f\) is the fraction of volume elements possessing jump sites. \(\Delta f = 1\) represents homogeneous flow, where all the volume elements of the sample undergo uniform flow. \(\Delta f \ll 1\) represents heterogeneous flow, where potential atomic jump sites are rather localized. The first exponential \(\exp(-\gamma v^* v_f)\) is derived by computing the probability of an atom to be on a potential jump site with Cohen and Turnbull theory [24, 25, 26]. The sinh term and the second exponential term are derived from a stress-biased activation energy model, as elaborated in [23]. The free-volume model of Spaepen is a thermal activation theory where the atomic jumps are caused by thermal fluctuations and biased by the external load.

In a subsequent work, Argon [3], developed a theory which identifies shear trans-
formations (ST) as the microscopic mechanisms behind plasticity in metallic glasses. STs are thermally activated. Argon suggested that there are two distinct modes of deformation in glasses. One is in the high-temperature regime \(0.6T_g<T<T_g\), where the STs are diffuse rearrangements of atoms. In the second mode, an ST takes place in a disk-shaped volume element involving a few \(<10\) atoms situated in two rows around a free volume region. The latter mode is generally seen at low temperatures and is analogous to the dislocation loop nucleation process in crystalline materials. Similar to the work of Spaepen, Argon assumed thermal-activation-based microscopic plasticity.

An alternative approach considered such STs as athermally activated. These STs were referred to as shear transformation zones (STZ) and the general theory referred to as effective temperature model. Langer and coworkers \([4, 27, 28, 29, 30, 31, 32]\) developed the effective temperature \(T_{\text{eff}}\) hypothesis which involved introducing a temperature term to describe the configurational disorder generated as a consequence of plastic-deformation-induced molecular rearrangements. The configurational disorder is a state where the configurational degrees of freedom fall out of equilibrium with the heat bath. When a sheared glass system is equilibrated at an effective temperature which is a function of the true temperature and the shear rate of the system, the fluctuations in the STZ density (or local energy) are comparable. Thereby the mechanical and thermal behaviour of a sheared glass can be described by introducing the effective temperature term. The effective temperature is higher than the true temperature and partly accounts for the mechanical description while shearing a glass sample. The authors further assumed that in a system which is in a thermodynamic nonequilibrium the STZ density converges toward \(n_{\infty} \exp (-1/\mathcal{X})\), where \(n_{\infty}\) is a density term signifying the number of molecules per unit volume. \(\mathcal{X}\) is expressed by \(k_B T_{\text{eff}}/E_Z\) where \(k_B\) is the Boltzmann constant, \(T_{\text{eff}}\) is the effective temperature and \(E_Z\) is the formation energy of the STZ. Effective temperature models are able
to describe the properties of metallic glasses that can be measured by experiments, such as the calorimetric behaviour of MGs [31].

b) The potential energy landscape concept

An atomic system comprising of $N$ atoms is represented by its $3N$-dimensional configurational space, where each atom has 3 configurational degrees of freedom. The atoms interact via a given interatomic potential. Thus, the potential energy of an atomic system is given by $V(R^{3N})$ where $R^{3N}$ represents the configurational degrees of freedom of $N$ atoms. The atomistic potential energy landscape (PEL) of the system is represented as the $3N$ dimensional surface in a $3N + 1$ dimensional space consisting of the configurational degrees of freedom and the energy axis. For a given potential, the PEL is a function of the interatomic potential and the boundary conditions. The phase of the system (such as amorphous or crystalline) is given by the region of the PEL where the system resides in. By exploring different regions of the PEL, interesting aspects of the material’s behaviour can be obtained.

The salient features of the PEL are compiled below:

- The PEL of a glass system contains numerous saddle-points and local minima. A saddle-point is a point in the PEL where at least one eigenvalue of the Hessian matrix is negative. The Hessian is the matrix of second derivatives of the potential energy with respect to configurational coordinates. In a given PEL, a saddle point is defined to be of a particular order depending on the number of negative eigenvalues of the Hessian at that point. The saddle-points of a PEL are of paramount importance because they represent the maximum energy of the minimum energy path between two local minima.

- The PEL of a glass system can be partitioned into basins encompassing each local minima of the PEL. Each local minimum in the PEL is connected to multiple saddle-points via a basin of attraction. The basin-of-attraction is defined
Figure 1.4: Schematic one-dimensional representation of the PEL of a glass-former depicting $\alpha$ and $\beta$-structural relaxation events, adapted from Harmon et al. [33].

as that region surrounding a local minimum from which, if the system is relaxed via the steepest descent or conjugate gradient method, the system relaxes to the local minimum associated with that basin.

In the undercooled liquids community, the PEL concept found relevance due to its direct relation to atomic-scale processes. In the paper by Johari and Goldstein [34], two types of relaxation mechanisms are believed to mediate glassy/undercooled liquid physics. One of them is the faster $\beta$-relaxation which involves atomic rearrangements of $\sim 10$ atoms. The second of the two mechanisms is the slower $\alpha$-relaxation, which involves reorganization of $\sim 40$ or higher number of atoms. A one-dimensional PEL depiction of these two mechanisms is shown in Fig. 1.4. The $\beta$-relaxations are reversible processes which are characterized by the transition of the system from a local minimum in the PEL of the glass system to another local minimum via a saddle-point. Such $\beta$-transitions are activated at low temperatures (well below the glass transition temperature $T_g$). In contrast, the $\alpha$-relaxations are irreversible processes that are frozen at temperatures below $T_g$. However at higher temperatures, the $\alpha$-relaxations are activated and the structural transformations are accompanied by the breakdown
of the surrounding elastic matrix. Collective $\beta$-activity is known to mediate an exit from an $\alpha$-megabasin as shown in Fig. 1.4. A complete traversal of an $\alpha$-hill is an irreversible process due to the complexity associated with reversing a larger $\alpha$-process. Thus the $\alpha$-mechanism is known to be responsible for macroscopic plasticity in glasses. Johari and Goldstein further argue that the transition from anelasticity (characterized by $\beta$-events) to plasticity (characterized by $\alpha$-events) involves a breakdown of the confining elastic matrix surrounding the inner $\beta$-processes. The irreversible $\alpha$ relaxation process involves the relaxation of a local elastic instability, which is mediated by multiple and reversible $\beta$ activity.

In the experimental investigation by Johari and Goldstein [34], the secondary relaxation mechanisms in viscous liquids was studied by experimental methods. Several liquid glass-formers were measured for their $T_g$ in this work. In the majority of them, the presence of a secondary relaxation mechanism was observed, in a temperature regime well below $T_g$. These observations were inferred from dielectric loss factor and dielectric permittivity measurements of the selected glass-formers. The authors claim that the secondary relaxation mechanisms are intrinsic properties of the liquids.

It is well-known that at a temperature closer to the glass transition temperature ($T_g$), there is only one type of relaxation mechanism that is accessible in the system. In this temperature regime, the other fundamental process that can take place is the diffusion between constituting atomic components. On decreasing the temperature, the thermal energy of the system drops. Consequently, some of the degrees of freedom of the atomic system are restricted. This results in the splitting of the relaxation mechanisms into $\alpha$ and $\beta$-relaxation mechanisms. The $\alpha$-relaxation is the primary relaxation mechanism which is completely frozen at low temperatures. The $\beta$-relaxation is the secondary relaxation process, which remains active even at extremely low temperatures, although hindered to some extent due to limited atomic motion caused by the drop in available thermal energy. The drop in temperature also leads to decou-
pling of diffusion between different atom types. At lower temperatures, the diffusion between larger atomic components slows down, whereas diffusion between smaller atoms still remains active. Thus, the natural question posed in this work is whether the onset of $\beta$-relaxation is in some way related to the differences in atom type. It is also important to note that for a liquid the two fundamental processes of diffusion and $\alpha$-relaxation are related by the Stokes-Einstein relation [35]. In the supercooled limit, however, this relation breaks down, which implies that the decoupled diffusive mechanisms cannot be so easily linked to the $\beta$-relaxation mechanism available at this temperature.

The materials science community has, however, associated microscopic plastic structural excitation events in glasses with the concept of STZ (Shear Transformation Zone) events, in contrast to the viewpoint of the undercooled liquids community where structural excitation events have been classified into $\beta$ and $\alpha$ transitions, [34]. The work of Harmon et. al. [33] was one of the first to bring this classification to the materials science community. This was subsequently discussed in the review in [2]. Ref. [33] notes that the smaller $\beta$-events are reversible whereas the large-sized $\alpha$-events are irreversible plastic events. The authors here argue that the transition from anelasticity to plasticity involves the breakdown of the confining elastic matrix surrounding the inner $\beta$-processes, which is characterized by an Eshelby backstress [36].

1.2.3 Simulation

a) Molecular dynamics simulations

The STZ model of Falk and Langer [4] is supported by high strain-rate molecular dynamics simulations. In their 1998 work, the authors investigated a two-dimensional binary amorphous system via molecular dynamics simulations. In that paper, the authors describe an STZ as a structural transformation which involves the rearrange-
ment of a group of atoms that relieve local stress. A diagram of an STZ is shown in Fig. 1.5. The figure depicts a local structural transformation of a group of four atoms which are shown to be encircled by an oval shaped representation. This region of the model system is denoted as an STZ. On application of shear stress (whose direction is shown by arrows), the oval shaped STZ which is elongated in the bottom-right to top-left direction prior to application of the shear stress transforms in such a way that the STZ is elongated in a bottom-left to top-right direction as a consequence of shear loading. Such a transformation is the STZ event. The atomistic simulations in this work confirm the presence of STZs in the model amorphous solid studied by the authors.

A major drawback of the molecular dynamics and static techniques employed is that it can only give a picture of stress-driven (athermal) mechanisms of deformation. This athermal regime of glass plasticity is a regime which is stress-driven and the effects of temperature are necessarily negligible and hence unaccounted for. This is due to the inherent limitation of molecular dynamics simulations, which run at very high strain-rates compared to experiments (up to 10 orders of magnitude higher).

In a 2004 letter by Maloney [37], atomic rearrangements in a model glass system were studied in the athermal limit, on application of quasistatic shear. The investigators used a soft-sphere potential [38] to model a 2D system. A quasistatic
algorithm was used to investigate the deformation behaviour in model amorphous systems. There, the authors reported to have discovered a quadrupolar structure of fluctuations in the potential energy of the system. Such fluctuations were seen between one single transition between two local minima. The authors further noted that there are cascade-like energy changes when the system transits between two local minima, which represents a typical plastic event. The second main finding in this work was the observation of elongated, crack-like events that percolate through the entire simulation box.

In the work of [39], three different three-dimensional model glass systems were studied, and uniaxial compression tests in these three systems were performed. Homogeneous deformation at higher cooling rates and heterogeneous deformation at slower cooling rates were observed. It was seen that the transition from high-temperature homogeneous flow to heterogeneous flow was indicated by a change in the sign of the strain-rate sensitivity from negative to positive, in the quasistatic limit as the quench rate was reduced. Short-range order (SRO) was determined in the three systems by the Frank-Kasper criterion. Additionally, the authors noted that extending from 2D to 3D does not alter the qualitative predictions regarding the features of the amorphous system.

Computer experiments to study deformation in amorphous silicon were conducted in [40]. In this work, molecular dynamics (MD) simulations were performed to plastically deform a model a-Si system interacting via the Stillinger-Weber (SW) potential. The full stress tensor was computed from the SW potential and the deviatoric part of the stress tensor was analysed for its distribution in the sample to locate individual plastic shear events. A drop in the deviatoric stress indicates a plastic shear event. The authors mentioned that the simulations were carried out at a low temperature of 300 K, to avoid any thermally activated atomic migrations. Samples were deformed beyond the yield strain via volume preserving plain-strain application. Four systems
with different densities were investigated in this work. It was found that the model sample with the lowest density showcases a yield point that is marked by an abrupt drop in pressure, i.e. strain softening. An explanation of such behaviour was given by the authors, who refer to the presence of solid-like and liquid-like environments in the sample, where the liquid-like regions are more susceptible to athermal plastic flow.

Subsequently the same authors [41] conducted further MD simulations on a model amorphous silicon (a-Si) system using the Stillinger-Weber potential. They formulated a single structure descriptor that could account for variations in a-Si density, coordination and stress distributions at the atomic scale. Based on it the material was characterized in two separate atomic environments, a solid-like and a liquid-like environment. The investigators further stated that a sample comprising of a higher fraction (denoted by $\phi$) of liquid-like environment is more susceptible to plastic flow. Such an observation indicates that the liquid-like regions are agents of athermal plasticity in amorphous systems. The paper noted that, on application of external stress, systems with different initial fractions of the liquid-like environment, i.e. systems with different initial $\phi$ values, tend to converge towards a steady-state plastic flow described by a unique value of $\phi$.

b) PEL exploration methods

Localized structural transformations in glass systems can be activated by thermal fluctuations. In a regime of glass plasticity, at low temperatures, thermal fluctuations drive the system from one stable local minimum to another in the PEL of the system. During such a transition the system passes through a saddle-point in the PEL. The transition rate is given by $\nu_0 \exp(-E_0/k_B T)$, where the prefactor $\nu_0$ is the attempt rate and $\exp(-E_0/k_B T)$ is the probability that such an attempt is successful, $E_0$ being the activation energy of the associated transformation. Detailed knowledge of
these two microscopic parameters is necessary to better understand the diverse range of thermally activated processes of different shape, size and energy-scales occurring throughout the sample.

There exist exploration methods to get out of a local minimum to a neighbouring saddle-point – they are referred to as potential energy landscape (PEL) exploration methods. A very successful method is the Activation Relaxation Technique nouveau (ARTn) [42, 43, 44], which is the method used in this thesis, see section 2.2.1 for a detailed explanation.

In the work of [45], thermally activated plastic events were studied using the (ARTn) technique. In this study, the authors investigated a 2D model Lennard-Jones system and deformed it via quasistatic shear. The distribution of the activation energies of the identified plastic events obtained by ARTn is shown in the left-hand panel of Fig. 1.6. The distribution is single-peaked at a finite barrier energy. A non-negligible percentage of low-energy barriers is seen in this distribution. The main results emerging from this paper is that there is a rise in the percentage of low-energy barriers on athermally deforming the sample (shown in the inset of the left panel of Fig.1.6). The plastic strains between the initial stable minimum and
the final stable minimum were computed and their distribution was found to peak at finite strain for the athermally deformed samples; see the right-hand panel of Fig.1.6. The distribution was seen to contain negative strain events. It was found that upon unloading the sample the mean plastic strain is non-zero and negative indicating a flow polarization. The plastic strains between the initial and final states showed no correlation with the activation energy of the events.

In a subsequent work by the same authors [46], a kinetic Monte Carlo (KMC) based ARTn technique was used to study the jamming-unjamming transition in a 2D model glass system. Here the end states and associated barrier energies were used as the kinetic pathways for the KMC. The loading was controlled by MC simulations and the minimum energy state of the glass obtained from the initial quench was tracked as a function of load increments before and after yield. In strain-controlled systems, the system is usually deformed in shear via application of Lee-Edwards boundary conditions on the atomic system. However, in order to compute the accurate yield stress, stress-controlled boundary conditions were required. Such an attempt led to capturing a yield point, which was lower by almost one-third of the yield stress computed from quasistatic simulation which were rather strain controlled. Thereafter, the ARTn technique was used to identify multiple elementary atomic rearrangements below and above the yield point of the glass system.

In a paper by [47], model a-Si systems were studied. Using the ARTn technique multiple saddle-points were identified in samples created with different degrees of relaxations, i.e. with different quench rates. The barrier-heights of the saddle-points, which are given by the energy differences between the saddle-points and the initial minimum, were studied for their distribution around the local minimum. Secondly, the energy differences between the saddle-points and their corresponding final states (a local minimum that is different from the initial minimum but connected to a given saddle-point) were denoted as reverse barrier-heights in this work and studied in
relation to the barrier-heights. It was found that there is no correlation of the reverse barrier-heights with the barrier-heights indicating that the two processes, namely, 1) the activation from the initial minimum to the saddle-point and 2) the relaxation from the saddle-point to the final minimum, are fairly independent of each other. One of the main results of this work was that the saddle-points derived from end-state configurations result in an exponential distribution of reverse barrier-heights, rather than a peaked distribution such as that found in \[45\]; see Fig. 1.6.

In \[48\], the authors identified $\sim 4000$ thermally activated structural transformations in a LJ glass sample by running the ART program on it. From the eigenfrequency of the Hessian matrix, the prefactor can be estimated via Harmonic Transition State Theory (hTST), \[49\]:

$$\nu^{\text{hTST}} = \frac{\prod_{i=1}^{3N-3} \nu^0_i}{\prod_{i=1}^{3N-4} \nu^*_{i-1}},$$

where $\nu^0_i$ and $\nu^*_{i-1}$ are the eigenfrequencies of the initial minimum and the saddle-point, respectively, which were computed by diagonalizing the Hessian matrix of the system at both points. The distribution of the prefactor was studied for varyingly quenched samples. In addition, the correlation between the prefactor and the activation energy was investigated. A very weak linear relation of the prefactor with the activation energy was found for some of the slowest quenched samples. This result was put in relevance with the Meyer-Neldel dependence of the prefactor with the activation energy \[50\], which is given by $\nu = \nu^0 \exp \left( \frac{E_A}{kT_0} \right)^\alpha$. The negative linear correlation found in this work is contrary to the Meyer-Neldel compensation rule \[50\], where the prefactor increases exponentially as a function of the activation energy. A surprising result found in this work was that the prefactor can vary by 10 orders of magnitude.

In the work of \[51, 52\] ART was used to study the statistics of saddle-point configurations in a model CuZr system as a function of quench rate. The authors found that the structural excitations predominantly involved atoms which had maximum relative displacements, compared to all atoms involved, denoted as trigger atoms. The
approximate relationship between these atomic displacements and their corresponding barrier energy was identified to be parabolic. Additionally, a linear/parabolic correlation between the change in local von Mises stress and the corresponding atomic displacement/activation energy was found. Strong deviations from the linear correlation between the von Mises stress and atomic displacements occurred mainly for the aforementioned trigger atoms. For less relaxed samples, the displacement of the trigger atoms were lessened, suggesting that the density of local minima in the glassy PEL increases. Indeed, the authors found that this had consequences for the final end state of the structural excitation, where for the more unrelaxed systems the resulting plasticity was cascade-like rather than localized and involved a larger number of atoms than that of the trigger atoms.

Other PEL exploration methods include parallel replica dynamics, hyperdynamics and temperature-accelerated dynamics [53]. In the parallel replica dynamics method, \(M\) replicas of an atomic configuration that resides in a basin in the PEL are generated on available parallel processors. On each processor, molecular dynamics is carried out on the replica configuration. When a rare event is identified on one of the processors, all the processors are stopped and the time for a rare event to occur is calculated as the cumulative time which is obtained by adding all the processor times at that instant. Such an approach is faster for detecting a rare event than running a molecular dynamics trajectory on just one processor. This method is easily parallelizable with only a few adjustable parameters.

In the temperature-accelerated dynamics method, the temperature of the system is increased to accelerate the dynamics. Such an approach facilitates the occurrence of transitions that would not have occurred at the initial temperature. These transitions need to be filtered out. At a high temperature, the escape paths and escape times of the transitions are determined. The system here obeys the harmonic Transition State Theory, where the transition rate has an exponential dependency on the barrier en-
ergy. Using this Arrhenius relation, the escape times for the transitions at the original low temperature can be extrapolated from the escape times at high temperature.

In the hyperdynamics method, a non-negative bias potential is added to the Potential Energy Surface (PES), which lowers the barrier-heights in the PEL. When molecular dynamics is performed on such a modified PEL, the system evolves from one state to another at an accelerated speed. The accelerated time-step is given by the product of the MD time-step and a boost factor. This technique ensures that the rate of transition is enhanced for each barrier crossing. Since the relative transition rates between two states do not change upon adding the bias potential, the evolution of the system from one state to another follows the same path as that of the unbiased MD trajectory.

A popular method to explore the atomistic PEL of a system is the metadynamics method which was first proposed in [54]. In this method, a bias potential is adaptively added to the Hamiltonian, often in the form of a Gaussian. The bias potential is a function of collective variables (CVs) identified, which are the descriptors of states in the system. For example, the collective variable can be potential energy, which describes whether the system is in a local minimum or is at a saddle-point. The bias potential added to a local minimum makes it more difficult for the system to return to this minimum after it has exited its basin of attraction.

The aforementioned dynamical simulation methods determine individual motion of atoms. Even though these methods are faster than the standard molecular dynamics technique, they do not fully overcome the challenges associated with finding the rare events which occur at a much larger time scale compared to the typical time scales of these methods. The real space nature of these methods limits their efficiency where events are based on atomic displacements. Working in the potential energy space is rather beneficial in terms of efficiency, where complex events can be generated by moving from a local minimum to a saddle-point [43]. The ART$n$ technique,
which is a PEL-based technique, overcomes this inherent difficulty in dynamical simulations by providing a strategy to directly capture such rare and complex atomic rearrangements, which involve simultaneous motion of many atoms without having to precisely follow the motion of individual atoms.

c) Thermal activation and kinetic Monte Carlo (KMC) methods

More generally, microscopic-based KMC models have been used to study thermally activated plasticity in glasses. In the early work of Bulatov & Argon [55, 56, 57], a mesoscopic model is proposed where plastic flow is treated as a stochastic sequence of local inelastic transformations (LITs). These LITs serve as the representative volume elements (RVEs) of plastic solids. With each new LIT occurring in the simulation all internal stress fields were recalculated. The average stress remained constant, but the total internal stress distribution evolved with time. The model successfully predicts diffuse high-temperature flow and localized low-temperature flow. More recent work is that of Homer & Schuh [58, 59]. A mesoscale model was proposed in [58], which employed the KMC algorithm to study the STZ activity as a Markov chain. The STZs were mapped onto a finite-element mesh and the distributions of stress and strain were computed at every step over the mesh. How the STZs interact with each other via the evolving heterogeneous stress distribution was a matter of interest in this work. Attempts to connect the atomic-level deformation mechanisms with continuum description of amorphous systems have been made by mesoscale modelling of the STZ mechanics in metallic glasses. Notable endeavours in this direction are the models proposed in [59]. This work coarse-grained the STZ event and used a kinetic Monte Carlo (KMC) algorithm to obtain enough STZ events. The macroscopic continuum response of the system was obtained by mapping the STZ events onto a 3D finite element mesh that can deform under shear in any of the 3-cartesian directions.
The model accurately predicts the high-temperature diffusive homogeneous flow and the low-temperature shear band localization, responses that are typical of amorphous systems. In all of the aforementioned mesoscopic models, [55, 56, 57, 58, 59], uncorrelated unit plastic events occur on application of low stress or strain-rate. Upon increasing the load, the unit plastic events interact with each other and organize themselves into localized groups of collective units, which together structurally transform to relieve the stress of the system leading towards macroscopic yield.

1.3 Background

A complementary effort to study glass plasticity has emerged between the condensed matter theory group at the Paul Scherrer Institute (PSI) and the Laboratory of Metal Physics and Technology (LMPT), ETH Zurich in the last few years. Particularly, experimental investigations carried out at ETH suggest that plastic flow in BMGs (via shear bands) is a thermally activated phenomenon [19, 20, 21, 22]. The current thesis investigates the underlying microscopic mechanisms which might lead to such thermally activated phenomena.

In the work in [19], a Zr-based bulk metallic glass was investigated for shear-band propagation. Particularly, the transition from serrated to non-serrated flow was related to shear-band characteristics, where serrated flow corresponds to discontinuities in the stress-strain curve. The smoothening of such discontinuities represents the aforementioned transition which the authors linked to the propagation of the shear-band. With a shear-band velocity range and a temperature range, Arrhenius behaviour was confirmed.

In a subsequent work [20], BMG plasticity involving shear bands was studied at cryogenic temperatures, i.e. at the low temperatures where inhomogeneous plastic activity dominates glassy physics. The nucleation rates of a shear band increases on reducing temperature, accommodating larger plastic strains. The authors of the
paper reported an increase in the strength of the BMG on reducing the temperature, which was explained via the viscosity of the single shear-band non-serrated flow. An important finding of this work was that the flow at such low temperatures is governed by just one shear band, contradicting results in past investigations which stated that there is an increase in shear-band activity at cryogenic temperatures.

It is a well-known fact that the arrest of shear bands takes place during the inhomogeneous serrated flow in BMGs. The work of [21] made an effort to understand the reason behind it by studying the transition from static to dynamic deformation in shear bands. This transition is accompanied by stress transients in terms of overshoots. The researchers analysed this process as a shear-melting transition and were able to measure the characteristic time for liquid-like to solid-like transformation in the shear band as a temperature-dependent measurable.

In a recent paper [22], different phases of shear-banding were discussed, including shear-band formation, propagation and arrest. Even creep and aging phenomena in shear banding were articulated, and the different time scales involved in shear-banding phases were discussed. The results may pave the way for controlled shear-band plasticity. The authors suggest that in serrated flow one stress-drop or a displacement jump corresponds to one full shear-band operation, which involves shear-band initiation, propagation and arrest. The experimental data illustrate that there is increased occurrence of unit plastic events corresponding to dilation at the shear-band initiation phase. In the next phase of shear-band propagation, the velocity of propagation is computed by differentiating the shear displacements with respect to time. The authors observe that shear-bands do not propagate at any time with a constant velocity; instead, they either accelerate or decelerate. The maximum velocity is reached at half of the stress drop for a particular serration, hence a deeper stress drop corresponds to higher shear-band velocity. The velocity quantity is of significant interest during shear-band propagation and has been thoroughly discussed in this work. Subsequent
phases, such as shear-band arrest, involve atomistic mechanisms such as reformation of broken bonds to regain the initial microstructure of icosahedra or specific SRO. On arrest, the material near the shear band freezes and becomes again solid-like and the shear-band velocity tends to zero.

In the aforementioned experimental investigations, an important observation was that there is no regime of glass plasticity where thermal activation can be avoided. In light of this, thermal activation models were proposed in Refs. [60, 61, 62] which complement the experimental findings.

In the thermal activation model proposed in [60], freezing below the glass transition temperature was modelled and a reproducible elastic to plastic transition was predicted. The yield point in BMGs is marked by a transition from a barrier-energy-dominated regime to a barrier-entropy-dominated regime in the elementary structural rearrangements. This transition allows the system to escape the “frozen” state. Based on this model, a yield criterion was developed that is validated by the experimental data.

In subsequent works [61, 62], a thermal activation model was used, which discusses a time-scale in which microscale plastic transitions occur in BMGs and the rate of such a transition event (1/τ) was computed. How the time-scale depends on stress and temperature was investigated. To find an expression for τ, two length scales were considered. The shorter length scale contains information on the heterogeneity of the transition events and the atomic structure. At a longer length scale, the material is structurally homogeneous. This is due to the fact that, with reference to the shorter length scale where distinct heterogeneous activities occur, the system is homogenized at the upper identified length scale. The model reproduced the onset of macroscopic yield at low temperatures well. At such temperatures, the complex PEL governing glassy physics is thermally inaccessible. To that end, the statistics of extreme value are employed in this work to analyze the distribution of barrier energies.
and the emergence of kinetic freezing. The response of the statistical framework under external load was also modelled. The model accounts for the transition to a high-temperature deformation regime in glasses, where homogeneous flow occurs, which can be described via thermally activated viscoplastic models.

1.4 Aims of the thesis

The aim of the thesis is an atomistic investigation of unit plastic processes in model LJ glasses, which are defined as the elementary atomic rearrangements underlying plasticity in glasses. In view of the strong evidence of thermally driven plasticity, structural excitations (here referred to as LSEs) will be studied, rather than stress-driven local instabilities. Using PEL exploration methods, one main goal of this thesis is to characterize these and to investigate their dependence on local structure. Finally, it is intended to study how the unit plastic processes respond to an external stress. Pertinent questions that are posed in this study are:

- How does the atomic structural environment of a unit plastic event correlate with its energy scale?
- What is the nature of the geometrical rearrangement of the unit plastic event?
- How is the distribution of the activation energy of the unit plastic event affected by an externally applied stress?
- How does the unit plastic event change in its structure and energy scale in the presence of an applied load?
1.5 Thesis outline

This thesis is organized into five chapters. After an introduction (chapter 1), the second chapter elaborates the numerical methods employed in this investigation. The numerical algorithms of molecular dynamics (MD) simulations, the activation and relaxation technique nouveau (ARTn) and the nudged elastic band (NEB) method are described. The MD simulations are used to generate model glass samples, whereas the ARTn and NEB techniques are employed to capture atomic-scale structural rearrangements in the generated glass systems and to obtain characteristic information pertaining to these rearrangements. The third chapter introduces the concept of local structural excitations (LSEs) in model glasses. The glass samples are characterized in terms of local atomic quantities (LAQs) and the correlation of the LSEs with their local atomic environment is studied. In the fourth chapter, the LSEs are investigated upon application of external load on the glass sample. The variation of LSE structure and energy scale is analyzed by applying different types of loading conditions. The fifth chapter summarizes the results obtained in this thesis and recommends future directions of investigation.
Chapter 2

Numerical methods

In this chapter, the numerical methods used in this thesis are discussed. Atomistic techniques such as molecular dynamics (MD), Activation Relaxation Technique nouveau (ARTn) and Nudged Elastic Band (NEB) method are employed for atomic-scale investigation purposes in glass systems.

2.1 MD: Classical Molecular Dynamics

2.1.1 Fundamentals

Classical molecular dynamics (MD) simulation is a numerical technique used to study atomic systems. In the framework of a classical MD set-up, each atom is defined by its atom type (mass, atomic number) and has a position and velocity. If there are $N$ atoms in the system, then a phase space consisting of $3N$ positional degrees of freedom ($r_1, r_2, ..., r_{3N}$) and $3N$ kinetic degrees of freedom ($v_1, v_2, ..., v_{3N}$) can be constructed where each atom has three positions and three velocity components in cartesian coordinates. Additionally, there is a force that acts on each atom due to its surrounding atoms. For an $N$-atom system the governing Newtonian equations of
motion are given by:

\[ F_i(r_1, r_2, ..., r_N) = m_i \frac{\partial^2 r_i}{\partial t^2}, \]  

(2.1)

where \( m_i \) is the mass, \( r_i \) the position, and \( F_i \) the force acting on atom \( i \). The time evolution of the positions can be calculated by numerically integrating eqn. 2.1. Numerical integrators used in this thesis are shown below, and are usually referred to as Velocity Verlet integrators [63]:

\[ x(t + \Delta t) \approx x(t) + v(t)\Delta t + \frac{1}{2} \frac{F(t)}{m} (\Delta t)^2, \]  

(2.2)

\[ v(t + \Delta t) \approx v(t) + \frac{F(t) + F(t + \Delta t)}{2} \Delta t. \]  

(2.3)

It is important to note that the total energy of the system during an MD simulation is conserved. The Hamiltonian of the \( N \)-body atomic system is given by:

\[ E = \frac{1}{2} \sum_{i \neq j} V_{ij}(r_i - r_j) + \sum_i \frac{p_i^2}{2m}, \]  

(2.4)

where \( p_i \) are the momenta and \( r_i \) are the position vectors of \( i = 1 \) to \( i = N \) atoms. The equations of motion given in eqn. 2.1 can be derived by differentiating the Hamiltonian with respect to degrees of freedom. A schematic diagram representing an MD algorithm is shown in Fig. 2.1
2.1.2 Modelling atomic interactions with potentials

In order to model interactions between atoms, interatomic forces are approximated by empirical potential functions. Usually, potentials found in literature belong to three broad types: a) pair potentials, b) embedded atom potentials and c) angular potentials. When the electrons in an atomic system are localized at the atomic positions, the interatomic interactions are best described by a pair potential given by:

\[ E = \frac{1}{2} \sum_{i,j,i \neq j} V_{ij}(r_i - r_j), \tag{2.5} \]

where \( E \) is the total potential energy of the system which is obtained by summing over the potential energy interactions between each pair of atoms. The interatomic potential between any two atoms is a function of only their atomic positions in this context.
A second class of potentials is the embedded atom potential (EAM), which best describes systems where the electrons are delocalized from the atoms, forming an electron cloud. In such cases, an extra density term is added which accounts for the binding energy of the electron cloud. An example expression of such a potential is shown below:

\[
E = \frac{1}{2} \sum_{ij, i \neq j} V_{ij}(r_i - r_j) + \sum_i F_i(\rho_i),
\]

\[
\rho_i = \sum_{j, i \neq j} \Delta \rho_j(r_i - r_j),
\]

where \(\sum_i F_i(\rho_i)\) is the binding energy of the electron cloud. Such potentials are mainly developed for metallic systems \([64, 65]\).

A third class of potentials is the angular potentials which model the interactions between atoms when electrons of atoms are localized at the bonds between atoms, as in covalent materials. An example expression of such a potential is:

\[
E = \frac{1}{2} \sum_{ij, i \neq j} V_{ij}(r_i - r_j) + \frac{1}{3!} \sum_{ijk, i \neq j, j \neq k} V_{ijk}(r_i - r_j, r_i - r_k, r_j - r_k).
\]

Such potentials are mainly used in covalent systems; see for example the Stillinger–Weber potential \([66]\).

In the present work, model glass samples were prepared by molecular dynamics and statics using a 50/50 binary mixture of a LJ system given by:

\[
V_{LJ}(r) = 4\epsilon \left( \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right),
\]

where \(\epsilon\) and \(\sigma\) set the microscopic energy and length scale of the model material. The parameterization used is that of Wahnström parametrization \([67]\), which is shown in Table 2.1. All simulation results are reported in LJ units, where time is measured with respect to \(\tau = (m\sigma^2/\epsilon)^{0.5}\), length in \(\sigma_{11}\) and energy in \(\epsilon\).
Table 2.1: Numerical values of the parameters of the LJ potential used in the thesis [67].

2.1.3 Nose-Hoover thermostat

In a classical MD simulation, the number, volume and energy of the system is usually kept constant representing an (NVE) microcanonical ensemble. However, in experiments, the number, volume and temperature (NVT) is kept constant which is known as the canonical ensemble. In order to control temperature in MD simulations, the most commonly used techniques that are adopted are velocity rescaling, Andersen thermostat, Nose-Hoover thermostat and Langevin dynamics. The Nose-Hoover (or the Anderson-Hoover thermostat) is a widely used thermostat in MD simulations [68, 69]. The corresponding Hamiltonian of the system when the simulation box is connected to a heat bath is given by:

$$ E = \frac{1}{2} \sum_{i,j,i \neq j} V_{ij}(\mathbf{r}_i - \mathbf{r}_j) + \sum_i \frac{p_i^2}{2m_i s^2} + \frac{p_s^2}{2Q} + (3N)kT\ln(s), \quad (2.10) $$

where $p_i$ are the virtual momenta and $\mathbf{r}_i$ are the position vectors of $i = 1$ to $i = N$ atoms, and $s$ is the additional degree of freedom of the heat bath. The actual momenta of the particles are given by $p/s$. $Q$ is the fictitious mass of the heat bath which
controls the degree of temperature fluctuations. The equations of motion can be derived by differentiating the Hamiltonian with respect to the degrees of freedom.

### 2.1.4 Parinello-Rahman barostat

Most laboratory experiments are performed under isothermal-isobaric conditions where in addition to a thermostat, a barostat is needed. Such an ensemble is known as the NPT ensemble. An extra dimension in the Nose-Hoover thermostat can be applied to pressure to formulate a Nose-Hoover barostat. More sophisticated techniques, such as Parrinello-Rahman methods, account for a change in the shape of the simulation box [70]. Here, the volume is a variable in the Parinello-Rahman simulations. The Hamiltonian of the Parinello-Rahman barostat is an extended version of the Nose-Hoover thermostat, although more complex in nature. The equations of motion can be derived from the following Lagrangian:

\[
L(s, h, \dot{s}, \dot{h}) = \sum_i m_i \dot{s}_i^T G \dot{s}_i + \sum_i WTr(\dot{h}, \dot{h}^T) - V(s, h) - p\Omega, \tag{2.11}
\]

where \(s_i\) is a position vector in fractional coordinates for atom \(i\), \(h\) is the matrix formed by lattice vectors, \(G\) is given by \(G = h^T h\), \(p\) is the external pressure, \(\Omega\) is the cell volume \((\Omega = |h|)\), and \(W\) is a constant of mass dimensionality.

### 2.1.5 Lee-Edwards boundary condition

In this thesis (see chapter 4), external shear is applied to a glass system by implementing the Lee-Edwards boundary condition [71]. The Lee-Edwards procedure imposes a shear-strain by using a shifted boundary condition. For example, for an XY shear-strain, atomic pairs crossing the periodic boundary along the y-axis are shifted along the x-axis by an amount equal to \(-\gamma L_y\). Here \(\gamma\) is the desired shear-strain and \(L_y\) is the box length along the y-axis.
2.2 ART\textsubscript{n}: Activation Relaxation Technique nouveau

(This section has been partly adapted from a technical report submitted by the author of this thesis in the framework of CCMX summer school held in Lausanne in 2012).

2.2.1 ART\textsubscript{n} algorithm

The ART\textsubscript{n} technique \cite{42, 43, 44} is the central tool of investigation in this thesis. It is a numerical technique that is employed in order to explore the atomistic PEL of a model glass system. The initial condition for ART\textsubscript{n} is a minuscule arbitrary displacement of a randomly selected atom. Given the displacement, the lowest eigenvalue of the Hessian corresponding to the deformation is computed where the Hessian is the double derivative of the total potential energy with respect to configurational coordinates, expressed as:

\[ H_{ij}(r) = \frac{\partial^2(V)}{\partial r_i \partial r_j}. \] (2.12)

Starting from a local equilibrium configuration, ART\textsubscript{n} converges to nearby saddle-point configurations of the PEL. The local minimum in which the glass system initially resides, is referred to as the initial state. A saddle-point directly connected to the initial state without any intermediary stable state in the path is referred to as the activated state corresponding to that local minimum. At the initial local minimum, all the eigenvalues of the Hessian matrix of the potential are positive. From there, in order to find the saddle-point configurations, ART\textsubscript{n} begins by perturbing the configuration a certain distance along a randomly chosen 3\textsubscript{N} dimensional direction or by displacing one atom in a random direction. The configuration is then moved stepwise in this random direction, relaxing total energy in the hyperplane perpendicular to the step direction in each iteration. This procedure is carried out until one of the eigen-
values of the Hessian matrix of the potential becomes negative. When this happens, the eigenvector corresponding to the lowest eigenvalue is selected and the system is moved in the direction of that eigenvector in steps of constant lengths. In order to diagonalize the Hessian matrix, the Lanczos scheme is employed which is described later in this chapter. At each of the iterations the forces perpendicular to the eigenvector are relaxed using the FIRE algorithm [72]. The FIRE algorithm is a numerical approach which is employed to relax the atomic coordinates. It involves adapting the molecular dynamics path by a modified velocity term and using adaptive time-steps. This method is faster than the traditional conjugate gradient method and is comparable with the quasi-Newton methods in terms of efficiency.

At the point of a negative eigenvalue, ART\textsuperscript{n} has climbed the local valley to an inflection region of the PEL. This part of the numerical procedure is referred to as the “destabilization phase” [46]. The “convergence phase” [46] of ART\textsuperscript{n} now involves a similar iterative procedure using the eigenvector associated with this negative eigenvalue, where at each iteration a new eigenvector is calculated. This is repeated until the projection of all forces along the eigenvector falls below a threshold and a saddle-point configuration is reached. This configuration is referred to as the activated state. In certain cases, the iterations are also stopped if the lowest eigenvalue becomes zero. In such a scenario, a translational mode has been identified which is responsible for most failures of ART\textsuperscript{n}. Another situation, where ART\textsuperscript{n} can fail corresponds to the lowest eigenvalue becoming positive. In that case, the system has fallen back into the initial minimum and the search is deemed unsuccessful. The success rate of ART\textsuperscript{n} is given by the percentage of saddle-points obtained from the total number of ART\textsuperscript{n} attempts, which is below 25% for all simulations conducted in this thesis.

A third phase of ART\textsuperscript{n} has been discussed in the paper of [46], which is the “relaxation phase”. In this phase the converged configuration at the saddle-point is perturbed in the phase space towards the initial local minimum. Subsequently, the
configuration is relaxed via molecular statics to check if the saddle-point is connected to the initial minimum. The saddle-points which are not connected are removed from the distribution. If the saddle-point is connected to the initial minimum, then it is perturbed in the phase space away from the initial minimum and is subsequently relaxed via molecular statics into a final state minimum.

A sketch of the ARTn method is shown in Fig. 2.2. It is emphasized that in this thesis it is assumed that ARTn provides an unbiased probe to nearby saddle-point configurations within the potential energy landscape — an assumption that underlies all previous work applying ARTn to glasses [45, 46, 47, 48].
Initial atomic config.

Randomly restart system by moving its coordinates in a chosen direction.

Build Hessian.

Lanczos scheme (QL with implicit shifts for diagonalization).

Obtain lowest eigenvalue.

Is the lowest eigenvalue negative?

Yes

Compute eigenvector corresp. to lowest eigenvalue.

Move system along the eigenvector relaxing all perpendicular forces.

No

Continue to move along the chosen direction relaxing all perpendicular forces.

Did the lowest eigenvalue converge?

Yes

Saddle point obtained.

No

Build Hessian.

Figure 2.2: Schematic representation of ARTn algorithm.
In order to find the eigenvector of the eigenvalue of the Hessian matrix, a Lanczos scheme is employed in the ARTn method. A numerical scheme for diagonalization of the Hessian significantly reduces the computational cost associated with a direct diagonalization. This procedure transforms the Hessian into a tridiagonal matrix by an orthogonal similarity transformation, as shown below:

\[ T = Q^T A Q \]  \hspace{1cm} (2.13)

Since \( T \) and \( A \) are similar, the eigenvalues and eigenvectors of \( A \) can be obtained by diagonalizing \( T \). This reduces the computational effort significantly.

The Lanczos method consists of constructing a series of converged tridiagonal matrices whose diagonal elements are denoted by \( \alpha_i \) and off-diagonal elements by \( \beta_i \). The Lanczos iterations are given as follows:

Given: \( r_0, \beta_0 = ||r_0|| \), where \( r_0 \) is a random non-zero vector, the following iterations are carried out until convergence:

\[ q_i = r_{i-1}/\beta_{i-1}, \]  \hspace{1cm} (2.14)

\[ r_i = A q_i - \beta_{i-1} q_{i-1}, \]  \hspace{1cm} (2.15)

\[ \alpha_i = q_i^T r_i, \]  \hspace{1cm} (2.16)

\[ r_i = r_i - \alpha_i q_i, \]  \hspace{1cm} (2.17)

\[ \beta_i = ||r_i||. \]  \hspace{1cm} (2.18)

Upon convergence, \( \alpha_i \) and \( \beta_i \) then represent the tridiagonal matrix which is to be diagonalized via the following QL method.
Diagonalization of the tridiagonal matrices is carried out by standard QL algorithms with implicit shifts. The QL algorithm refers to a method of finding the eigenvalues of the Hessian matrix $A$. The Hessian matrix $A$ can be decomposed into $A = QL$ where $Q$ is an orthogonal matrix and $L$ is lower triangular. Considering the matrix formed by writing the factors in reverse order, we get $A = Q L$. Since $Q$ is orthogonal, $A = Q L$ implies $L = Q^T L$. The QL algorithm consists of a sequence of orthogonal transformations, $A_{s+1} = Q^T A_s Q$. Standard theorems prove that, as $s$ tends to infinity, $A_s$ tends to triangular form with eigenvalues on the diagonal in increasing order of magnitude.

In the above formulation $A_s$ is tridiagonal and $Q$ is orthogonal. The convergence of a superdiagonal element $a_{ij}$ is given by the ratio $\frac{\lambda_i}{\lambda_j}$, where $\lambda_i$ are the eigenvalues of $A$. This convergence can be improved by a shifting technique. If $k_s$ is any constant, then the eigenvalues of $A - k_s 1$ are $\lambda_i - k_s$. The convergence is then given by $\frac{\lambda_i - k_s}{\lambda_j - k_s}$. $k_s$ is manipulated to maximize the rate of convergence. The QL algorithm with implicit shifts is known as the QL algorithm which does not require $k_s 1$ to be actually subtacted from $A$. The shift $k_s$ enters implicitly through the parameters involved.

### 2.2.2 ARTn parameters

To find a saddle-point configuration, ARTn begins by moving the configuration a certain distance along a randomly chosen $3N$-dimensional direction. Here, this direction is chosen by first randomly selecting an atom and then randomly moving it a distance $0.15 \sigma_{11}$. The configuration is then moved along the eigenvector with the lowest eigenvalue in steps of $0.025 \sigma_{11}$ until the eigenvalue is less than $-3.0 \epsilon / \sigma_{11}^2$. At each stage, the forces perpendicular to the eigenvector are relaxed. The above procedure is continued now using a variable step size of $F.u_0 / \epsilon_0$, where $F$ is the current $3N$-dimensional atomic force vector and $u_0$ is the $3N$-dimensional eigenvector corresponding to the lowest eigenvalue $\epsilon_0$. This step size is capped at $0.125 \sigma_{11}$.  

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This is repeated until the maximum force on all atoms is less than $10^{-3} \epsilon/\sigma_{11}$. These parameters are used for all the ARTn simulations in the current thesis.

2.3 NEB: Nudged Elastic Band method

2.3.1 MEP: Minimum Energy Path

In the atomistic PEL of a glass configuration, the relevant path that connects the initial stable minimum and the final stable minimum is known as the minimum energy path (MEP). The salient features of the MEP are mentioned as follows:

• The reaction coordinate of a transformation is the relative distance along the MEP from a starting state PEL minimum to an end state PEL minimum.

• The maximum along the MEP is a saddle-point which represents an equilibrium configuration of relative stability. At a saddle-point, the direction of the reaction coordinate is given by the direction of the eigenvector corresponding to a negative eigenvalue.

• A MEP can have more than one maximum, i.e., saddle-points corresponding to metastable states. However, the rate of a transformation between the end states is governed by the highest saddle-point. It is therefore necessary to have knowledge of the shape of the MEP in order to calculate the rate, in addition to locating the saddle-points on the path.

• The saddle-points on a MEP can be of first or of higher order. A first-order saddle-point is a maximum along one degree of freedom and a minimum along the remaining $3N - 1$ degrees of freedom. Similarly, a $k$-order saddle-point is known to be a maximum along $k$ degrees of freedom and a minimum along the remaining $3N - k$ degrees of freedom. To locate a first-order saddle-point, it is
therefore required to maximize forces along one degree of freedom and minimize the forces along the remaining degrees of freedom. To this end, an efficient method used extensively in recent literature [73, 74, 75, 76] is the nudged elastic band (NEB) method, which is described in the following sections.

2.3.2 NEB algorithm

The NEB method constructs the MEP between an initial state and a final state by creating a set of intermediate images (or replica configurations: \([R_0, R_1, ..., R_N]\)) of the atomic system between the two limiting states, where \(R_0\) and \(R_N\) are the initial state and the final state, respectively. The number of images is usually of the order of 4 to 20. The images interact via spring forces between neighbouring images which promotes continuity of the path. The path thus models an elastic band. Minimizing relevant forces acting on the elastic band results in its convergence onto the MEP.

The total forces acting on an image is the sum of the tangential spring force and perpendicular true force. An expression for the total force is given by:

\[
F_i = F_i^s \parallel - \nabla E(R_i) \perp, \tag{2.19}
\]

where the true force is \(\nabla E(R_i) \perp\), which can be expanded into

\[
\nabla E(R_i) \perp = \nabla E(R_i) - \nabla E(R_i) \hat{i}, \tag{2.20}
\]

and the spring force \(F_i^s \parallel\) can be expressed as:

\[
F_i^s \parallel = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|) \hat{i}, \tag{2.21}
\]

where \(k\) is the spring constant and \(\hat{i}\) is the unit tangent at the image under consideration. A simple estimate for the unit tangent can be numerically computed from the position vectors of the two adjacent images, \(\hat{i} = \frac{R_{i+1} - R_{i-1}}{|R_{i+1} - R_{i-1}|}\).
Thus using the NEB method, which requires the initial state and the final state configuration, the minimum energy path (MEP) is constructed, which is the lowest energy path connecting the initial and the final state. The NEB method generates several intermediate configurations (known as images) along this path, relaxing all forces of each image which are perpendicular to the local MEP tangent as well as maintaining a continuity of the MEP via connecting springs to each $3N$ dimensional image configuration. One of the intermediate configurations corresponding to the maximum energy along the MEP is the desired saddle-point or the activated state. The schematics of the NEB algorithm is shown in Fig. 2.3.

![NEB Algorithm Schematic](image)

**Figure 2.3: Schematic representation of NEB algorithm**

### 2.3.3 NEB parameters

- **Spring constants:** The images on the MEP between the initial and the final state interact via spring forces. This is required in order to ensure the continuity of
the path. However, it is necessary to obtain higher accuracy of the tangents near the saddle points. In such cases, stronger springs are used near the saddle point for better resolution. It is pertinent to mention that different strategies can be adopted to distribute the springs unevenly if the approximate shape of the path is known in advance. One can in fact choose different spring constants between each pair of images, since the spring forces that distribute the images on the MEP do not affect the true forces. In this thesis equal spring constants of values $100, 150$ and $200 \frac{\epsilon}{\sigma_{11}^2}$ are used.

- Number of images: To obtain accurate activated states representing a true saddle-point configuration (as found by ART$n$) via NEB, a large number of images are necessary. Such an approach makes the NEB method computationally expensive. A cost-effective and faster way to obtain such saddle-point configurations with the desired accuracy is to use NEB with a small number of intermediate images and then to interpolate to the exact saddle-point configuration. In the current thesis, the number of images of $9, 19, 29$ and $39$ are used.

A parametric study of MEPs of structural excitations is carried out in chapter 4.
2.4 Sample preparation

The sample preparation involved three steps: 1) Equilibration of the atomic configuration by NPT molecular dynamics at a temperature of $10000 \times k_B [\varepsilon/k_B]$ and hydrostatic pressure of $8/160 [\varepsilon/\sigma_{11}^3]$ to generate the liquid state; 2) slow quenching of the sample from the pressurized and well-equilibrated liquid state, which involves an incremental reduction in temperature ($-198.0 \times k_B [\varepsilon/k_B]$) and pressure ($-0.158/160 [\varepsilon/\sigma_{11}^3]$) by NPT molecular dynamics to form the disordered amorphous glass at a temperature of $100 \times k_B [\varepsilon/k_B]$ and hydrostatic pressure of $0.1/160 [\varepsilon/\sigma_{11}^3]$; and 3) relaxation of the atomic coordinates to zero temperature and zero hydrostatic pressure by molecular statics using the Parrinello-Rahman method [70]. For steps 1 and 2 the Parrinello-Rahman [70] barostat was used for pressure control and the Anderson-Hoover [77] thermostat was used for temperature control. This procedure was also used in the work of ref. [78].

Although a number of samples were constructed in this way – see Table 2.2, this
<table>
<thead>
<tr>
<th>Quench Rate (↓) / no. of atoms (→)</th>
<th>1728</th>
<th>13834</th>
<th>110592</th>
<th>884736</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_1 = 24.57/500$</td>
<td>0a</td>
<td>1a</td>
<td>2a</td>
<td>3a</td>
</tr>
<tr>
<td>$\eta_2 = 24.57/5000$</td>
<td>0b</td>
<td>1b</td>
<td>2b</td>
<td>3b</td>
</tr>
<tr>
<td>$\eta_3 = 24.57/50000$</td>
<td>0c</td>
<td>1c</td>
<td>2c</td>
<td>3c</td>
</tr>
<tr>
<td>$\eta_4 = 24.57/500000$</td>
<td>0d</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 2.2: A tabular chart of glass samples prepared in this thesis as a function of system size and quench rate.

thesis will mainly focus on using the smaller samples and in particular 0d. Past work [78] has shown that when a low enough quench rate is used, the structural statistics differ little between samples. Unpublished work (private communication with Dr. Peter Derlet) also demonstrates that the statistics and nature of the LSEs obtained from ARTn do not differ for larger samples.
Chapter 3

Local structural excitations at zero applied load

The goal of this chapter is to investigate the statistics of the local atomic environment in which an LSE exists in terms of a variety of local atomic quantities. This is largely motivated by past work which introduces the idea of “liquid-like” regions more susceptible to plastic activity. This chapter details the work of the published research paper “S. Swayamjyoti, J. F. Löffler, and P. M. Derlet, Local structural excitations in model glasses, Phys. Rev. B 89, 224201 (2014)” and its corresponding archive version “S. Swayamjyoti, J. F. Löffler, and P. M. Derlet, Local structural excitations in model glasses, 2013 arXiv:1311.6640v1 [cond-mat.soft]”.

3.1 LAQs: Local Atomic Quantities

The local quantities (the LAQs) being considered are

- atomic volume
energy

• pressure

• dilation elastic modulus (three times the local bulk modulus)

• the five linearly independent Kelvin eigen-shear elastic moduli

3.1.1 Atomic volume

The local volume of an atom is defined here as the volume of the corresponding voronoi cell derived from a voronoi tessalation of the structure. The program used to do this is voro++ [79]. In an atom packing, the voronoi cell of an atom is constructed such that any point inside the voronoi cell is closer to that atom than any other atom. Voronoi volume changes during an atomic rearrangement can lead to insights about its role in facilitating such rearrangements.

3.1.2 Potential energy

The local atomic potential energies can be straightforwardly calculated from the interatomic LJ potentials, with which the atoms interact. For a pair potential \( V(R) \), the local potential energy is given by

\[
E_i = \frac{1}{2} \sum_j V(R_{ij}),
\]

where the summation refers to the sum over neighbours within the interaction range of the potential. The sum is halved due to each bond contributing half of its energy to the local potential energy.

3.1.3 Pressure

For a pair potential \( V(R) \), the local stress tensor can be computed in a similar manner to that described in [78]:

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\[ \sigma_{a}^{\mu\nu} = \frac{1}{2V_a} \sum_{ij} V'(R_{ij}) \frac{R_{ij}^{\mu} R_{ij}^{\nu}}{R_{ij}} \Lambda_{a,ij}. \]  

(3.2)

In the above expression, \( \Lambda_{a,ij} \) represents the proportion of the \( ij \)th bond \( (R_{ij}) \) within the volume of atom \( a \). It is noted that bonds between two atoms, neither of which is atom \( a \), may also contribute to these two local quantities. Eqn. 3.2 properly partitions volume and therefore correctly takes into account the contribution of each atomic bond [80, 81]. The local pressure is obtained by taking one-third the trace of the local shear stress tensor:

\[ P_a = \frac{1}{3} Tr[\sigma_{a}^{\mu\nu}]. \]  

(3.3)

3.1.4 Eigenshears

Kelvin local eigenshear moduli are intrinsic properties of a material system [82] and are obtainable by diagonalizing the Kelvin elastic stiffness tensor of a generalized anisotropic material. Kelvin notation is an alternative to the commonly used Voigt notation of the \( 3 \times 3 \times 3 \times 3 \) elastic stiffness tensor. In contrast to the Voigt matrix, the Kelvin matrix preserves the norm of the actual elastic stiffness tensor and hence its eigenvalues and eigenvectors have geometrical significance [83]. Since the Kelvin notation has a tensorial form, the eigenvalues of the stiffness matrix can be computed to obtain the bulk modulus and the five linearly independent eigenshear moduli. The invariance of these eigenshear moduli with respect to coordinate systems and thereby their role as an intrinsic material property was highlighted in [82].

Of particular interest to the authors are the negative local eigenshear moduli. In a global context, ref. [83] mentions that the physical realization of a stiffness matrix requires its Kelvin eigenvalues to be non-negative. In a local context, negative eigenshear moduli are believed to be in the regions of the glass sample which are prone to local structural transformations. Atoms with negative eigenshear moduli are believed to be involved in local plastic events (microscopic structural transformations) [84].
Since a LJ pair potential is being used, the expression for the local elastic stiffness tensor is:

\[ C_{\mu\nu\alpha\beta}^a = \frac{1}{2V_a} \sum_{ij} \left[ V''(R_{ij}) - \frac{V'(R_{ij})}{R_{ij}} \right] \times \frac{R_{ij}^\mu R_{ij}^\nu R_{ij}^\alpha R_{ij}^\beta}{R_{ij}^2} \Lambda_{a,ij} \]

\[ + \sigma_{\mu}^{\nu\beta} \delta_{\mu\alpha} + \sigma_{\nu}^{\mu\alpha} \delta_{\mu\beta}, \]  

(3.4)

where \( \Lambda_{a,ij} \) has the same meaning as in [78].

To obtain the Kelvin elastic moduli [85] from the fourth rank elastic stiffness tensor (eqn. 3.4), the usual Voigt elastic stiffness matrix is first constructed, from which the Kelvin matrix (2nd rank tensor) is obtained via \( C_K^{\mu\nu} = A^{\mu\nu}C_V^{\mu\nu} \). For an explicit form of \( A^{\mu\nu} \), see ref. [78]. The five linearly independent eigen-shear moduli are obtained by first projecting out the pure dilation distortions (which give the local bulk modulus) and then diagonalizing the resulting Kelvin matrix — for more details, see refs. [78, 84].

### 3.2 Analysis methodology

#### 3.2.1 Weighted atomic displacement technique

The distributions of the local atomic quantities involved in LSE events have been studied in relation to the distributions of these quantities in the total sample. To this end, the weighted mean atomic quantity corresponding to each LSE event is computed as follows.

A typical LSE event involves a transition from the total initial relaxed state to the activated state in the PEL of a glass sample, by overcoming the barrier energy. At a configurational level, this leads to the rearrangement of \( N_{\text{LSE}} \) atoms, where \( N_{\text{LSE}} \) is the number of atoms involved in that LSE. The magnitudes of displacement vectors of each atom \( i \) is denoted by \( |\Delta R_i| \). Consequently, the local weight is computed as:

\[ w_i = \frac{|\Delta R_i|^4}{\sum_{i=1}^{N} |\Delta R_i|^4}, \]  

(3.5)
where the weights are chosen such that they are normalized to unity, that is, \( \sum_{i=1}^{N} w_i = 1 \), for a given LSE event, where \( N \) is the total number of atoms in the sample.

The local atomic quantities are weighted by the weights computed above, and the weighted mean of each atomic quantity is considered as an atomic quantity of that LSE. The formulation chosen above ensures that the weighted mean atomic properties of the LSE event are biased towards the atomic properties of atoms which have higher displacements in the LSE event. Atoms with negligible displacements are automatically neglected in the weighted mean computations as the corresponding weights are quite small. The weighted mean property of a LSE is thus calculated as:

\[
LAQ_{\text{LSE}} = \sum_{i=1}^{N} (w_i \times LAQ_i),
\]

where LAQ stands for Local Atomic Quantity and can be one of the local properties under study, i.e. Voronoi volume \( (V) \), potential energy \( (E) \), pressure \( (P) \), bulk modulus \( (BM) \) and the five eigen-shear moduli \( (ESM1, ESM2, ESM3, ESM4, ESM5) \). The distributions of the \( LAQ_{\text{LSE}} \) are statistically analysed in the next section to gain insight into the microscopic events otherwise known as LSE events.

### 3.2.2 Participation number

In the context of the present study, participation number \( (PN) \) is the effective number of atoms participating in an LSE event [86]. This number is defined in terms of the weights of the atoms involved in a particular LSE event. The participation number employed in the present work is given by:

\[
PN = \frac{1}{\sum_{i=1}^{N} w_i^2},
\]

where \( N \) is the total number of atoms in the sample and the local weights are defined as in eqn. 3.5

The participation number varies between \( 1 \) and \( N \). The value of PN is 1 when just one atom has moved. The weight of this atom is 1 and the weights of other atoms
are zero. The value of PN is $N$ when the weights are equally distributed between all atoms in the sample. In this case, all atoms in the sample have moved by the same distance and hence all atoms have equal participation.

### 3.2.3 PCC: Pearson correlation coefficients

Pearson correlation coefficient (PCC) is a correlation coefficient [87], which quantifies the linear dependence between two variables. This coefficient is given by

$$PCC = \frac{\sum_{i=1}^{n}(X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^{n}(X_i - \bar{X})^2} \sqrt{\sum_{i=1}^{n}(Y_i - \bar{Y})^2}}, \quad (3.8)$$

where $X_i$ and $Y_i$ are the datasets, and $\bar{X}$ and $\bar{Y}$ are the arithmetic means of the $X_i$ and $Y_i$ datasets respectively, with $i$ the data number ranging from 1 to $n$. PCC ranges from $-1$ to $1$, where the values $-1$ and $1$ refer to complete linear correlation. A Pearson coefficient value of 0 indicates no linear correlation at all. In the present study, the correlation between weighted averaged local atomic quantities of atoms involved in an LSE have been studied against the activation energies of these LSE events. Scatter plot analysis and Pearson coefficient values provide a comprehensive picture of correlation between local atomic quantities and barrier energies.

### 3.2.4 Natural Mode Analysis

The natural modes of an $N$ atom configuration can be obtained via the solution to

$$\sum_{j}^{\mu\nu} (m_i [\omega_n]^2 \delta_{ij} \delta^{\mu\nu} - \Delta_{ij}^{\mu\nu}) u_{j,n}^{\nu} = 0, \quad (3.9)$$

where $\Delta_{ij}^{\mu\nu}$ is the translationally invariant dynamical matrix obtained from

$$\Delta_{ij}^{\mu\nu} = \sum_{a,a \neq i} H_{ia}^{\mu\nu} \delta_{ij} - H_{ij}^{\mu\nu} (1 - \delta_{ij}). \quad (3.10)$$

Here $H_{ij}^{\mu\nu}$ is the Hessian. In terms of the LJ interaction, $V(r)$, the Hessian may be written as

$$H_{ij}^{\mu\nu} = \left[V''(R_{ij}) - \frac{V'(R_{ij})}{R_{ij}}\right] \frac{R_{ij}^{\mu} R_{ij}^{\nu}}{R_{ij}^2} + \frac{V'(R_{ij})}{R_{ij}} \delta^{\mu\nu}. \quad (3.11)$$
In eqn. 3.9, $m_i$ is the atomic mass of the $i$-th atom, and $u_{j,n}^\nu$ is the eigen-vector associated with the eigen-frequency $\omega_n$ of the $n$th natural mode. The number of atoms participating in a particular eigenstate, $u_{j,n}^\nu$, may be obtained via the participation number [86]

$$\text{PN}_n = \left[ \sum_i |\vec{u}_{i,n}|^4 \right]^{-1},$$  

(3.12)

where $\vec{u}_{i,n}$ is the three-dimensional polarisation vector of atom $i$ coming from the eigenvector of eigenfrequency $\omega_n$. Assuming a normalised eigenvector, $\text{PN}_n$ will range between unity (when the eigenstate is concentrated on just one atom) and $N$ (when the eigenstate is distributed evenly over the entire sample). The natural modes give information about the vibrational properties of the structure.

### 3.2.5 Uniqueness of ART\textit{n}-generated saddle points

To avoid redundant saddle-point configurations, converged activated states whose barrier energy differs by less than $0.001 \epsilon$ from any other activated state are further inspected. If the centre-of-positions of the LSEs (derived from the $3N$-dimensional atomic displacement vectors between the initial and activated state) is less than $0.001\sigma_{11}$, then the configuration is discarded.

### 3.3 Results

#### 3.3.1 Barrier energy and participation number statistics

The 4262 unique activated states present were identified using the ART\textit{n} method. To verify that each activated state was directly connected to the initial atomic configuration, the activated configuration was perturbed in a direction towards the initial atomic state configuration and allowed to relax. If the resulting structure differed from the initial structure the LSE was discarded from the dataset, as was done in
Figure 3.1: Red balls represent the centre-of-positions of all identified local structural excitations and the green balls represent regions containing free volume within the simulation cell of the model glass.

Ref. [45]. In a similar way, the final state could be determined by perturbing the activated configuration in a direction away from the initial atomic state configuration and allowed to relax.

Fig. 3.2a displays the distribution of barrier energies obtained from the 4262 identified activated states for the sample with the slowest quench rate. In agreement with Refs. [45, 46, 47, 48], the distribution peaks at a non-zero barrier energy and appears to approach zero for small enough barrier energies. The barrier energy scale is comparable to that seen in a previous fully three-dimensional ART\textsubscript{n} simulation using the same LJ potential parametrisation [48]. Inspection of the participation number in
Fig. 3.2b reveals that the effective number of atoms involved in the LSE is typically less than ten and that the LSEs with barrier energies in the lowest and highest regime involve only a few atoms. Close inspection of the final state participation number (see inset to Fig. 3.2b) reveals a clustering at integer values of the participation number. This does not occur for the activated state configuration demonstrating that while the non-affine displacement field associated with the activated configuration is dispersed over many atoms, the non-affine field of the final state can be localized on a discrete number of atoms. Further inspection of all LSEs revealed that 389 initial/activated/final state atomic configurations had the feature that the final state configuration had an identical total energy to the initial state. Detailed inspection of these LSEs revealed that in these 389 cases, the final state involved a permutation of nearby atoms of the same type, where the activated configuration involved a closed loop of displaced neighbouring atoms (see Fig. 3.11a for an example). Thus the final state is identical to the initial state and when not included in Fig. 3.2b the discrete participation numbers vanish. Since such LSEs cannot produce any strain these were also removed from the dataset used in the LAQ analysis.

Fig. 3.2c now displays a histogram of the participation numbers indicating that the LSEs identified by ARTn generally involve one to several atoms. Thus on average there is little difference in the number of participating atoms between an activated and a final-state. On the other hand, Fig. 3.2d displays the difference in participation number between connected activated and final-state configurations, showing that the number can either decrease or increase by several atoms. On average, however, the change in the participation number is close to zero indicating no strong bias as to whether the final state contains more or fewer participating atoms than the activated state, a result compatible with Fig. 3.2c.

To determine the spatial location of a particular LSE, the centre-of-position of those saddle-point atoms displaced relative to the initial configuration by more than
Figure 3.2: a) Normalised distribution of activation energies of LSEs in a 3D model glass system. b) Scatter plot of participation number (PN) of activated and final state configurations versus activation energy, where the inset is a blow-up of the final-state configuration participation numbers. c) Histogram of participation number and d) scatter plot of participation-number difference between the connected activated and final states as a function of activation energy.

0.1σ was calculated. Fig. 3.1 displays these positions within a boundary box defining the three-dimensional periodic simulation cell. A general inspection of their spatial distribution reveals some heterogeneity and, in particular, regions where many LSEs are similarly located. A more detailed inspection of such LSEs (as in a manner

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described in sec. 3.3.7) reveals them to be quite different in spatial extent and barrier energy, despite some LSEs having their centre-of-position almost coincident. The goal below is to see whether any local structural feature correlates with this observed heterogeneity.

### 3.3.2 Histograms of LSE-weighted LAQs

Fig. 3.3 displays the normalised histograms of a number of LSE-averaged LAQs with respect to the activated and final state configurations; also shown are the equivalent unweighted histograms derived from the total sample. The two types of distributions will be referred to as LSE-weighted and unweighted distributions of the LAQ. For the unweighted distributions the (atom-type resolved) partial histograms are also shown.

Fig 3.3a represents the normalised distribution of potential energy of atoms. The double-peak structure of the total unweighted distribution is clearly seen to arise from the single-peaked distributions of each atomic type. The LSE weighted distributions, on the other hand, do not exhibit a double-peak structure, with the single observed peak coinciding with the unweighted partial distribution of atoms of type 2. This result suggests that the atoms involved in an LSE are often of type 2. Fig. 3.3b now shows the corresponding normalised distribution for the Voronoi volume. Inspection of the unweighted curves shows that atoms of type 2 have lower volume compared to atoms of type 1, a feature that is expected given the nature of the Wahnström parametrization (see table 2.1 and ref. [78]). The distinct double-peak feature is, however, absent for the LSE-weighted distributions, both the activated and final state curves showing a single-peaked structure approximately centred between the unweighted partial distributions. Closer inspection does, however, reveal a slight bias to the lower volumes of the type 2 atoms. Figs. 3.3c and d show the distributions for both local pressure and local bulk modulus, respectively. For both LAQs, the unweighted total distribution shows single-peaked curves that are slightly asymmetric.
Figure 3.3: Normalized distribution of local a) energy, b) volume, c) pressure, and d) bulk modulus. The red vertical lines represent the corresponding mean value derived from the total sample.

due to slightly different contributions from the two atom types. That atoms of type 2 are involved in the LSEs is also reflected here because the LSE-weighted curves are more biased towards the partial unweighted curves of type 2 atoms.

Fig 3.4 shows the distribution of Kelvin eigen-shear moduli for the activated and final relaxed states. Again, the unweighted total and partial distributions are shown for comparison. It is noted that for each atom, the local Voigt matrix is first constructed via eqn. 3.4, from which the local Kelvin matrix is built and is then diago-
Figure 3.4: Normalised distribution of five local eigenshear moduli where a) to e) represents the lowest to highest values. The red vertical lines represent the corresponding mean value derived from the total sample.
nalized (after the dilation components are projected out), to obtain five eigen-shear moduli. These are then ordered and each order is binned separately to produce the five panels of Fig. 3.4. As seen in ref. [78], the left tail of the distribution of lowest eigenshear moduli extends into the negative moduli domain. That some atoms have a local distortion characterised by a negative modulus does not entail a local material instability because their calculation involves only those neighbouring atoms with a direct interaction and not the stabilising effect of the more distant surrounding matrix. Such low or negative eigenshear moduli do, however, indicate the presence of local shear distortions that are soft. Inspection of the unweighted total and partial LAQ single-peak distributions reveal that atoms of type 2 are slightly biased towards regions of softer moduli. The weighted LAQ single-peak distribution follows this bias, confirming that atoms of type 2 are often involved in an LSE.
3.3.3 Scatter diagrams depicting correlations of LAQs with LSE activation energy

Figure 3.5: a) Normalised distribution of LSE-weighted atom types for the activated and final state configurations and b) scatter plot of participation number vs. LSE-weighted atom-type.

To gain more direct information on the type of atom involved, normalised atom type LSE-weighted distributions were generated. Fig. 3.5a displays these for both the activated states and the final states. Both distributions peak at the average atom-type of 1 and 2, and for intermediate values there is essentially a flat distribution with a slight bias towards LSEs with higher average atom-type. This suggests that the most probable specific chemical composition will consist of only type 2 atoms, however on average an LSE will contain a mixture of both atom types with a bias towards atoms of type 2. Inspection of those LSEs containing only atoms of type 2 reveals them to consist of mainly one or two atoms. On the other hand, LSEs containing a mixture of both atom-types can consist of many more atoms. This is demonstrated in Fig. 3.5b, which shows the scatter plot of participation number with LSE-weighted atom-type. Here there is a clustering of small LSEs around atom-type 75.
2, but many larger LSEs consisting of both type 1 and type 2 atoms are evident. The lower boundary in this figure reflects the fact that for an average atom-type of 1.5 at least two atoms must be involved.

**Figure 3.6:** Scatter plots of LSE-weighted local a) energy, b) volume, c) pressure, and d) bulk modulus vs. activation energies.

Fig. 3.6 displays scatter plots of the LSE-weighted LAQs with respect to their corresponding barrier energy. Data are shown for local cohesive energy, volume, pressure and bulk modulus. Inspection of these figures reveals strong scatter and no strong linear correlation. This is evidenced by the associated Pearson correlation coefficients shown in table. 3.1. The exception to this trend is that of the local cohesive energy,
which has a Pearson correlation coefficient equal to approximately -0.5, indicating a non-negligible linear correlation with the barrier energy. Fig. 3.7a – e shows similar scatter plots for the five Kelvin eigenshear moduli. Little correlation is again evident, although the Pearson correlation coefficient for the lowest eigenshear modulus is approximately 0.25, with the value progressively decreasing with increasing eigenshear number; see table 3.1 which lists these coefficients for all five moduli. What causes these weak correlations? A closer inspection demonstrates that the origin is again atom-type, where those LSEs with atoms predominantly of type 2 are not only more common, but also appear to correspond to lower barrier energies. This is seen directly in Fig. 3.7f, which is a scatter plot of atom-type and barrier energy. This plot again shows that there is a bias towards LSEs with a majority of type-two atoms, with the corresponding barrier energies being on average slightly lower than the barrier energies associated with LSEs dominated by atoms of type one. The scatter associated with this trend is, however, large with the spread in barrier energy comparable to the domain of the distribution shown in Fig. 3.2a, for both types of LSEs.
Figure 3.7: Scatter plots of LSE-weighted local eigenshear moduli vs. activation energies from a) lowest to e) highest value. f) Scatter plot of atom-type and activation energy.
Table 3.1: Pearson Correlation Coefficients (PCCs) representing the correlation between local atomic quantity and activation energy.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Activated State PCC</th>
<th>Final Relaxed State PCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>0.1593</td>
<td>0.1039</td>
</tr>
<tr>
<td>E</td>
<td>-0.4793</td>
<td>-0.4897</td>
</tr>
<tr>
<td>P</td>
<td>0.1264</td>
<td>0.0084</td>
</tr>
<tr>
<td>V</td>
<td>0.0821</td>
<td>0.0522</td>
</tr>
<tr>
<td>ESM1</td>
<td>0.2850</td>
<td>0.2473</td>
</tr>
<tr>
<td>ESM2</td>
<td>0.2170</td>
<td>0.1703</td>
</tr>
<tr>
<td>ESM3</td>
<td>0.1611</td>
<td>0.1343</td>
</tr>
<tr>
<td>ESM4</td>
<td>0.1051</td>
<td>0.0461</td>
</tr>
<tr>
<td>ESM5</td>
<td>0.0506</td>
<td>0.0154</td>
</tr>
</tbody>
</table>

3.3.4 Excess free volume: a facilitator of LSEs

To determine the spatial location of free volume within the computer-generated sample, the simulation cell is filled with a fine regular cubic mesh of points, at a spacing much smaller than the typical inter-atomic distance of $\sim \sigma$. Those mesh points that have a distance to the nearest atom greater than $R_{\text{max}}$, and which are connected to each other, will then define the spatial extent of a region of local free volume. $R_{\text{max}}$ cannot be too small, because then the normal interstitial regions, which span the entire simulation cell, will be identified. The parameter should also not be too large since then no free volume will be identified. Such a method has been used to identify free volume in grain boundaries [88]. Using a value of $R_{\text{max}} = 0.76\sigma$, Fig. 3.1 displays the identified regions as green balls. This figure shows that the computer-generated sample contains a few regions in which local free volume is above the normal background of interstitial regions.

Fig. 3.8 now shows a histogram of $R_{fv}$, i.e. the nearest distance of a LSE centre-
Figure 3.8: Distribution of minimum distances between the centre-of-position of an LSE and free volume in the sample. For comparison similar distributions are shown for the case when LSEs are distributed randomly throughout the simulation cell.

of-position (the red coloured balls in Fig. 3.1) to all identified free volume (the green coloured balls in Fig. 3.1). Also shown are histograms of four random realizations of LSE centre-of-positions derived from a uniform distribution within the simulation cell. Inspection of this figure shows a slight bias of the ARTn identified LSEs to be closer to free volume than that of entirely randomly located LSEs. Thus there exists some correlation between the location of an LSE and nearby free volume.

### 3.3.5 Correlation with vibrational modes

Fig. 3.9a shows the plot of the “vibrational participation numbers” (eqn. 3.12) against eigenvalue numbers corresponding to each eigenstate, where the vibrational participation number represents the effective number of atoms participating in a vibrational eigenmode. Here the eigenvalues have been sorted from smallest to largest and therefore the horizontal axis is proportional to increasing vibrational frequency. Such data have been calculated before [78, 89, 90, 91], demonstrating that at low frequencies
the eigenmodes are strongly heterogeneous indicating quasi-localized mode behaviour that is believed to underlie the well-known Boson peak phenomenon of disordered systems [92, 93, 94, 95, 96]. At the highest frequencies the participation number drops again reflecting a localization that is understood within the framework of Anderson localization [97, 98, 99, 100]. To investigate any correlation between the existence of such low-frequency quasi-localized and high-frequency localized modes, the overlap between the vibrational eigenstate and that of the LSE was determined. This was done by calculating the scalar product of the atomic weights (eqn. 3.5) with the eigenvector magnitude-squared, $|u_{i,n}|^2$. Fig. 3.9b displays both the average overlap and the maximum overlap of all identified LSEs with each vibrational eigenmode.

The figure shows that there exists, on average, little overlap over the entire frequency range. In the low-frequency regime, the average overlap is a well-defined statistical quantity, indicating that irrespective of the nature of the quasi-localized mode, the spatial location and extension of the identified LSEs are similar for different modes. This is also reflected in the maximum overlap which varies little with eigenstate, and is also a small quantity. At higher frequencies the situation is somewhat different in that there is much more scatter in the average value and the maximum value. This, however, does not indicate any important correlation because the small average and large maximum values more likely indicate the scenario that statistically there will be one or some LSEs that do not strongly overlap with one or some well-localized high-frequency eigenstates. This does not occur at the low-frequency quasi-localized eigenstates because these are more extended, involving several tens to hundreds of atoms (see Fig. 13 of ref. [78]). Thus the current analysis reveals little correlation between the spatial extent of the vibrational modes and the location of the LSEs identified.
3.3.6 Effect of quench rates

The ART$n$ simulations were also performed on glass samples prepared using faster quench rates (sample 0a with $\eta_1$, sample 0b with $\eta_2$, sample 0c with $\eta_3$; see table 3.10), and a comparative study was performed to determine whether the results depend on the quench rate. Fig. 3.10a displays the resulting activation energy distributions, showing that for the more rapidly quenched systems the peak of the distribution shifts to lower activation energies and that close to the zero activation energy limit, the distribution does not reduce to zero (a result also seen in the work of Rodney and Schuh [45, 46]). Fig. 3.10b now shows the participation number distribution (eqn. 3.7), revealing that with increasing quench rate there is a slight shift to a larger number of atoms being involved in the LSEs and that many of these involve a more mixed number of atom type — see Fig. 3.10c, which displays the average atom-type distribution of the LSEs. These results are compatible to that of recent studies by [51, 52]. They also suggest that the more rapidly the model system is quenched, the more shallow the local potential minimum is, and that the corresponding LSEs are somewhat larger, involving both types (sizes) of atom. In general, however, the
weak correlation with local structural features is insensitive to quench rate. For example, Fig. 3.10d displays the LAQ-weighted lowest Kelvin eigenshear distribution as a function of quench rate, which displays only a slight shift towards lower elastic stiffness moduli.

Figure 3.10: Panels showing the effect of different quench rates in which the fastest quench rate is sample 0a and the slowest is sample 0d. a) Histograms of the activation energy; b) the participation number; c) the atom type; and d) the lowest Kelvin eigenshear distribution.
3.3.7 Atomic-scale visualization of LSEs

In this section, six identified LSEs are atomistically visualized. These examples were chosen because they represent typical features seen in all LSEs. They are shown in Fig 3.11. In all of the examples, the initial and final atomic positions are represented by green and orange spheres, respectively, whereas the red arrows represent the displacement from the initial to activated position and the blue arrows the displacements from the activated to final position. Only those atoms are shown which are displaced by more than $0.2\sigma$, either between the initial and activated, or the activated and final configuration. The large spheres represent atoms of type 1 and the small spheres atoms of type 2. Generally, the visualised atoms may be classified into two groups, those central atoms that involve significant and irreversible displacement and those atoms that accommodate this activity either via reversible elastic or irreversible plastic displacement. In all figures, the first class of initial atom positions is numbered, with the dashed-corresponding-number labeling their final position.

Fig. 3.11a represents an LSE with an activation energy of $11.98\epsilon$ involving 8 atoms. In this LSE, the central atomic structure forms a symmetrical ring-like (or closed chain-like) structure ($1 \rightarrow 1'$ : $2 \rightarrow 2'$ : $3 \rightarrow 3'$), consisting mainly of smaller atoms (of type 1). Surrounding this plastic inner structure, there are mainly larger atoms (of type 2) which move back and forth during the initial to activated state and then from the activated to final state transition, respectively. This is also an example of elastic accommodation mechanism around the inner ring-like plastic rearrangement. In this case, the LSE results in a final configuration identical to the initial configuration apart from a permutation of three labels. Such LSEs (numbering 389) have been removed from the statistical analysis performed in sec. 3.1.
Figure 3.11: Six examples of local structural excitations identified by ARTn. In each case the initial atomic positions are visualized by green balls and the final ones by orange balls. The atomic displacements from the initial to activated and activated to final states are visualized by red and blue arrows, respectively.
Fig 3.11b represents an LSE with an activation energy of 6.65ϵ involving 17 atoms. It shows an extended chain-like atomic motion with the sequence being specified by (1 → 1’ : 2 → 2’ : 3 → 3’ : 4 → 4’). Although smaller atoms (of type 2) are involved in the formation of the chain, there is a relatively large number of large atoms (of type 1) that are responsible for accommodating this structural excitation. There is evidence of both elastic and plastic accommodation by the surrounding atoms, which is clearly seen by atoms moving back and forth as well as atoms moving irreversibly in the region surrounding the inner chain-like formation. From this LSE (and also confirmed in the subsequent descriptions of LSEs), it is observed that excitations which involve a higher number of atoms in the chain-like structure also involve a proportionally higher number of atoms in the surrounding accommodation mechanisms.

Fig 3.11c represents an LSE with an activation energy of 10.35ϵ involving 9 atoms. It also shows a chain-like atomic reconfiguration, now of a strongly curved extension. The sequence is specified by (1 → 1’ : 2 → 2’ : 3 → 3’ : 4 → 4’ : 5 → 5’). Here both atom sizes are involved in the re-configuration. This was also the case for the surrounding elastic accommodation, where both types of atoms were involved.

One of the most spatially extended LSEs identified by ARTn is shown in Fig. 3.11d. This LSE has an activation energy of 16.01ϵ and involves 17 atoms, where the reconfiguration sequence, (1 → 1’ : 2 → 2’ : 3 → 3’ : 4 → 4’ : 5 → 5’ : 6 → 6’). It is noted that smaller atoms (of type 2) are involved at both ends of the chain sequence, and that both types of atoms are involved in the elastic and plastic accommodation. Such mixed atom-type chain-like activity is also seen in the smaller ring-like LSEs as shown in Fig. 3.11e, which has an activation energy of 10.55ϵ. Finally, Fig 3.11f represents an LSE with an activation energy of 8.96ϵ involving 11 atoms. This LSE forms a chain (1 → 1’ : 2 → 2’ : 3 → 3’ : 4 → 4’) which almost resembles a straight line due to its low curvature.

Upon inspection of these figures, the chain-like sequence of an LSE generally
involves one atom replacing its neighbour (and so on), such that the chain or part of
the chain is fully connected (with respect to the red and blue displacement arrows). In
addition, one atom can move to a previously unoccupied location, with another atom
doing the same with respect to another atom (and so on), forming a disconnected
chain (with respect to the red and blue displacement arrows). The smaller ring-like
structures of Figs. 3.11a and e fall into the first category and the extended chains
fall into both categories. Very low-energy LSEs were also visualized (not shown)
and these tended to involve just one atom changing its location with minor elastic
and plastic accommodation in the surrounding regions. Such LSEs typically have
activation energies in the range of less than \( \sim 5\varepsilon \).

### 3.3.8 Shape number

Fig. 3.11 demonstrates that LSEs can be spatially extended. To better quantify this
observation, a non-dimensional quantity derived from the radius of gyration is used.
The radius of gyration (which is also commonly used in molecular applications) in
the present context is given by:

\[
R_g = \sqrt{\frac{1}{N_{\text{LSE}}} \sum_{k=1}^{N_{\text{LSE}}} (\mathbf{r}_k - \mathbf{r}_{\text{cop}})^2},
\]

where \( N_{\text{LSE}} \) is the number of atoms involved in the LSE, \( \mathbf{r}_k \) is the position of the
concerned atom and \( \mathbf{r}_{\text{cop}} \) is the centre of position of the LSE. The dimensionless
shape number is then defined as \( R_g/R_{\text{max}} \), where \( R_{\text{max}} \) is the maximum distance from
the centre-of-position of an atom within the LSE. The shape number is computed
using the initial positions of the atoms involved in the LSEs. An atom is considered
to be part of the LSE if its displacement (at the activated state) is greater than 0.3 Å.
This cut-off was used to exclude the surrounding accommodating atoms (which have
relatively smaller displacements), thus ensuring that only the central atoms within
the LSE are considered.
Figure 3.12: a) Shape number distribution derived from all identified LSEs; b) scatter plot of shape number vs. participation number; c) shows the relationship between LSE size and shape number for the two limiting geometries of a linearly extended LSE and a randomly spatially distributed LSE; d) scatter plot of activation energy vs. shape number.

Fig. 3.12a displays the histogram of shape numbers derived from all of the LSEs identified. To understand this figure, some limiting cases of the shape number formalism are first considered. When only one central atom is involved in an LSE, the shape number becomes indeterminate and when two atoms are involved the shape number reaches its largest value of unity. An LSE consisting of an arbitrary number of atoms
all situated on the surface (perimeter) of a sphere (circle) also gives a value of unity. Fig. 3.12b displays the shape number as a function of $N_{\text{LSE}}$ for the cases of a perfect linear chain and a spherical volume in which the positions of the atoms are chosen randomly. The data corresponding to the latter case also include the converged standard deviation. In Fig. 3.12a, the peak at a shape number of unity is either due to a strong population of perfect rings containing an arbitrary number of atoms or the many two-atom LSEs discussed previously. Inspection of Fig. 3.12c, which plots the scatter diagram of participation number vs. shape number, demonstrates the latter case, where there exists a dense line of LSEs with a participation number of approximately two at a shape number of one. For larger LSEs, Fig. 3.2c shows that typical participation numbers are between 3 and 5. In this regime, the shape numbers for the limiting cases of Fig. 3.12b reach values between 0.7 and 0.85, which is precisely the location of the central peak in Fig. 3.12a. Fig. 3.12c shows that LSEs consisting of greater than five atoms have shape numbers spanning the entire range of possible values, indicating that both extended and more compact LSE structures contribute to the peak in Fig. 3.12a, a conclusion compatible with Fig. 3.11. The enhanced tail at low shape numbers does suggest larger extended LSE chains. Importantly, in most cases an LSE may be characterized by an approximate sequence of atoms replacing other atoms, rather than a random rearrangement of atomic positions. Fig. 3.12d displays a scatter graph of the activation energy vs. shape number, showing that there is little correlation between the spatial extension of an LSE and its barrier energy.

3.4 Discussion

The results of sec. 3.3 suggest that the location of an LSE is only weakly correlated with the local structural features of those atoms involved. For the LJ system considered, the only non-negligible correlation is that the smaller atoms of type 2 are more often involved than the larger atoms of type 1, particularly when the LSEs consist
of only a few atoms and are at the lower range of the activation energy spectrum. Despite the strong scatter, this latter aspect suggests a rather intuitive scenario where type two atoms generally involve less negative bond energies. The breaking of bonds that must occur in an LSE requires less energy and therefore lower activation energy. Indeed this appears to be more important than local Voronoi volume. Fig. 3.3b shows that the volume LSE-weighted distribution exhibits only a central peak structure not located at volumes typical of type 2 atoms, whereas the local cohesive energy LSE distribution clearly correlates with the type 2 unweighted peak (Fig. 3.3a). The remaining, somewhat weaker correlation with activation energy is that a small or negative lowest local Kelvin eigenshear tends to have a low activation energy. This is again an intuitive result since a small or negative Kelvin eigenshear indicates a shallow potential energy minimum and therefore a smaller activation barrier. In other words, the LSEs occurring in softer regions tend to have lower activation energies.

The atomistic visualization shown in sec. 3.3.7 generally demonstrates LSEs to be a sequence of atoms that successively replace each others’ approximate locations, with the surrounding atoms accommodating such movement through either elastic or plastic distortion. This appears to be a general result, although the spatial extension of the atomic sequence can be quite diverse, ranging from an almost linear extension to strongly curved and closed ring-like structures (for the smaller LSEs). It is found that nearby free volume is correlated with their existence. The investigation for any correlation with nearby free volume is motivated by the original assumption of Spaepen in his thermally activated free-volume theory [23].

A relevant question is to which class of relaxation processes ($\alpha$ or $\beta$) should the identified LSEs belong to. Fig. 3.13a displays a histogram of the change in energy between the initial and final atomic configurations found by ART $n$. In most cases, this energy is positive, with a few LSEs leading to a decrease in energy and therefore a more stable atomic configuration than the initial configuration reached by dynamic
Figure 3.13: a) Normalized distribution of the change in energy between the initial and final state configurations and b) a scatter plot of this energy difference with the corresponding activation energy.

atomistic simulations. Given that only LSEs are considered which have a direct path between the initial and activated states (that is, there exists no intermediate stable configuration), Fig. 3.13a suggests that the initial configuration is in the basin of a much larger PEL valley and therefore in the valley of the $\alpha$ landscape. From this context, the ART$n$ appears to primarily probe the $\beta$ PEL involving the first LSE stage that would generate the atomic configuration’s journey out of its current $\alpha$ mega-basin. Fig. 3.13b shows the scatter plot of the corresponding activation energy vs. the change in energy between the initial and final atomic configurations. The plot demonstrates the obvious fact that an activated energy cannot be less than the final-state energy for LSEs that are directly connected to the initial state. The figure also reveals that those final states that have an energy less than the initial state are separated by the full spectrum of possible activation energies, with only very few final states having small activation energies. Generally, little correlation is seen apart from the observation that both energy scales are comparable, demonstrating that, if the assumed surrounding $\alpha$ energy landscape does exist, the underlying “ripple” $\beta$
energy scale is that of the LSE energy scale. Thus β processes may not be so sensitive to their local environment whereas no such statement can be made for α processes. Fig. 3.11 shows, however, that identifying LSEs as β processes has the consequence that bonds are broken for the latter — a result that differs from the view-point that only α processes involve the breaking of bonds (see, for example, Ref. [2] and references therein). Clearly further work is needed to confirm this picture.

The next chapter investigates how the picture is modified via the application of load.
Chapter 4

Local structural excitations at non-zero applied load

The goal of this chapter is to investigate LSEs under applied external load. Fresh ARTn runs are carried out on strained glass samples to collect statistics for LSEs under load. Additionally, the data obtained from ARTn simulations in chapter 3 are used for further investigations under load by employing the NEB method, which is systematically applied to the strained start and end state configurations of individual LSEs. This chapter details the work of the published research paper “S. Swayamjyoti, J. F. Löffler, and P. M. Derlet, Local structural excitations in model glass systems under applied load”, Phys. Rev. B 93, 144202 (2016).”

4.1 Loading conditions and strain control

LSEs are investigated under tensile, compressive, and pure shear loading conditions via a static distortion of the simulation cell. For the tensile loading geometry, fractional volume changes of 0.00525, 0.0105, 0.01575, and 0.021 are considered where
upon each volume change the amorphous structure is relaxed. Similar negative volume changes are applied to investigate the compressive loading geometry. The motivation for both protocols is to investigate any tension/compression asymmetry that might arise in the statistics of the corresponding LSEs.

A pure shear loading is applied by imposing the Lee-Edwards boundary conditions [71] on the simulation cell. The samples are sheared to incremental shear-strain values of \(2 \times \text{shear strain} = 0.003, 0.006, 0.009, 0.012, 0.015, 0.018, 0.021, 0.024, 0.027, \) and 0.03. For each shear strain the atomic coordinates are relaxed. The XY, YZ and ZX shear planes are considered.

### 4.2 Stress-strain relationship

![Stress-strain relationship](image)

Figure 4.1: a) Stress-strain relationship for tensile and compressive loading. b) Stress-strain relationship for shear loading in XY, YZ and ZX planes.
For the straining geometries and associated strain magnitudes, the corresponding global stress tensor, $\tau^{\mu\nu}$, can be calculated via

$$\tau^{\mu\nu} = \frac{1}{2V} \sum_{ij} \phi' (R_{ij}) \frac{R_{ij}^{\mu} R_{ij}^{\nu}}{R_{ij}},$$

which is valid for a pair interaction $\phi(r)$ such as the Lennard-Jones potential. In the above equation, $V$ is the volume of the simulation cell and $R_{ij}$ is the inter-atomic distance between atoms $i$ and $j$. Fig. 4.1a shows the plot of the pressure against isotropic strain. It is seen that the global hydrostatic pressures varies predominantly linearly as a function of strain increments, where the weak non-linearity is due to the expected volume asymmetry in tension and compression. Fig. 4.1b shows a similar plot of the shear stress against the shear strain for XY, YZ and ZX loading geometries. The shear stress shows extended linear behaviour as a function of strain. The derivative of these curves gives the corresponding elastic moduli. Under isotropic tensile/compressive deformation, the resulting bulk modulus is found to equal 75.8 $\epsilon/(\sigma_{11})^3$, whereas the shear moduli for the XY, YZ and ZX geometries are found to equal 21.8, 21.1, and 20.5 $\epsilon/(\sigma_{11})^3$, respectively. These results compare well with the values found in past work [78]. Inspection of Fig. 4.1 reveals that zero pressure configuration does not have fully relaxed global shear stresses. This turns out not to be a serious deficiency of the sample since differences in total energy and internal stresses are always considered. Indeed, as shown below, the differences seen in the XY, YZ and ZX shear data are found to be statistically irrelevant.

### 4.3 Methodology of ARTn and NEB investigations of LSEs under load

Here the ARTn technique is employed for the strained samples in a way similar to that in chapter 3. Thus barrier energy statistics can be investigated as a function of
strain. To investigate how individual LSEs respond to imposed strain a combination of NEB and ARTn is used to follow the barrier energy as a function of strain. This entails usage of NEB to first obtain an approximate MEP of the structural excitation. To obtain, via NEB, accurate activated states reflecting a true saddle-point configuration (as found by ARTn), a very large number of image configurations is needed. This makes the NEB method computationally expensive. A more efficient method of obtaining such saddle-point configurations is to use NEB with a smaller number of intermediate images and then to use that image with the maximum energy as a starting configuration for the ARTn procedure. The ARTn-converged configuration should then result in a true saddle-point configuration. Due to the complex nature of a glassy PEL, a high density of saddle-point configurations is expected. Such a scenario entertains the possibility that the converged saddle-point configuration at a particular strain might be different to that of earlier strains. In this study, to reduce such possibilities, both the barrier energy and negative eigenvalue (curvature of the saddle-point) are followed as a function of strain, and the LSE as a function of strain is only complete when these quantities do not deviate abruptly.

4.3.1 LSEs not connected to the initial minimum

In chapter 3, the distribution of LSEs was analysed under zero load conditions for the presence of saddle-points that were not connected to the initial minimum. To gain information on whether the saddle-points collected are directly connected to the initial minimum configuration from which ARTn is run, without any intermediate saddle-point in the path, the configuration is relaxed via molecular statics on either side of the saddle-point. The two local minima that are obtained via this strategy are investigated to check whether one of them is the initial minimum. If a saddle-point is not connected to the initial minimum then it is removed from the dataset. However, the statistics of the saddle-points that are not directly connected to the start
state and of those that are directly connected are not much different – see Fig. 4.2. Hence, it is assumed that this is also the case under finite loading conditions and such saddle-points are allowed to remain in the dataset. Not checking for the direct connection is done to avoid the huge computational cost of running molecular statics simulations for thousands of saddle-points obtained from ARTn at different strains.

It is now checked whether new intermediate states emerge in the ∼ 400 LSEs which were individually tracked using the combined NEB and ARTn approach – (see sec. 4.4) and in all cases no true intermediate barriers emerged – (see sec. 4.4.5).
4.4 ART\textsuperscript{n} and NEB analysis of LSEs under load

4.4.1 Shear strain distortions

In Figs. 4.3a to c the normalised distributions of the barrier energies obtained by ART\textsuperscript{n} are displayed for the XY, YZ and ZX shear-strains. The distributions are derived from several thousand saddle-points for each shear plane. For each geometry two shear-strain magnitudes plus zero applied load are shown. The figures reveal that the overall distributions change very little as a function of applied shear-strain. Detailed inspection of the data does, however, reveal a weak broadening and downward shift of the distribution by a scale less than $\varepsilon$ (this can also be observed in Fig. 4.6a, which plots the mean of the barrier energies obtained). The origin of this trend is best seen by inspecting how the barrier energies of the individual LSEs change with respect to the applied shear by using the combined ART\textsuperscript{n} and NEB approach outlined in sec. 4.3. Fig. 4.3d displays a plot of the change in barrier energy versus shear-strain applied in the XY plane for a number of representative LSEs. The figure demonstrates that depending on the particular LSE the corresponding barrier energy can either increase or decrease, where for the considered strain magnitudes the maximum barrier energy change is of the order of $\varepsilon$. Similar trends are seen for the YZ and ZX loading geometries.

The picture which therefore emerges is that under pure shear-strain loading geometry, a particular barrier energy may either increase or decrease. This is further confirmed by performing a similar NEB/ART\textsuperscript{n} analysis for several hundred LSEs. It is found that the distribution of change in barrier energy, as a function of shear-strain magnitude, is distributed over positive and negative values, but biased towards a decrease in the barrier energy. This trend will be later quantified through investigating the distribution of resulting activation volumes – see sec. 4.4.3.

In Figs. 4.3a and c, for the XY and ZX shear geometries, a small peak in the low-
Figure 4.3: Normalized distributions of barrier energies obtained via ARTn for a) XY, b) YZ, and c) ZX pure shear-strains for two strain magnitudes. In all figures the distribution for the zero-load sample is also included. d) Barrier-energy evolution as a function of XY shear stress magnitude (shear strain × appropriate shear modulus) for several individual LSEs derived via a combination of ARTn and NEB.

A barrier-energy regime is seen to emerge as a function of increasing strain magnitude. Inspection of the structure of the saddle-point configurations which correspond to these low barrier energies reveals that they arise from LSEs involving the same single atom. Thus, in this case, ARTn converges a disproportional amount of times to the same LSE, but with a slightly different saddle-point configuration. This indicates a very broad and low barrier energy saddle-point structure, and may be seen as a
4.4.2 Isotropic strain distortions

Figs. 4.4a and 4.5a show the barrier-energy distributions obtained via ART$n$ as a function of both compressive and tensile isotropic strain. Again, the overall distributions do not greatly change as a function of strain. However, closer inspection reveals that for the compressive and tensile cases, the distribution shifts to higher and lower barrier energies, respectively. There is also a weak broadening in both cases. These trends are quantified in Figs. 4.6a, which shows the mean barrier energy as function of volume strain. The origin of this trend is again seen by inspecting how the barrier energy changes as a function of strain for individual LSEs. Figs. 4.4b and 4.5b plot such data for some representative LSEs, where for compressive/tensile loadings the LSE barrier energies generally increase/decrease.
Figure 4.5: a) Normalized distribution of barrier energies obtained via ART\(n\) as a function of isotropic tensile strain. The distribution for the zero-load sample is also included. b) Barrier energy evolution as a function of isotropic tensile stress magnitude (isotropic tensile strain \(\times\) bulk modulus) for several LSEs derived via a combination of ART\(n\) and NEB.

4.4.3 Summary of results – general trends and activation volume

The main findings from the analysis of LSE distributions under load is that the barrier energies increase in compression and decrease in tension. Under pure shear, the barrier energies can either increase or decrease, with a slight bias towards a lowering of the barrier energies. These trends are reflected in Fig. 4.6a, which depicts the variation in average barrier energy as a function of applied strain. These data are an average of the three shear geometries. The figure shows a clear increase/decrease during isotropic compression/expansion and only a weak decrease under pure shear strain, where for the latter case Fig. 4.3 indicates that the dominant effect is a broadening of the distribution.

To quantify these trends, the activation volumes of the LSEs are considered, and the relation of the barrier energy with respect to applied stress is discussed. Historically, the stress dependence of a thermally activated plastic process has been
understood in terms of a stress-dependent barrier energy [18, 101]. The simplest parametrization of such a dependence is obtained by assuming that the barrier energy is a linear function of the applied stress $\tau$:

$$E(\tau) = E(\tau = 0) - \Omega \tau,$$

(4.2)

where $\Omega$ has the unit of a volume. This term is referred to as the activation volume and is an important material parameter for thermally driven plasticity. For an isotropic applied strain, the appropriate $\tau$ is a hydrostatic pressure and the activation volume is always positive, reflecting the fact that barrier energies decrease/increase upon material dilation/compression. For the case of pure shear strain, it will be shown, however, that a barrier energy may either decrease or increase and thus the activation volume can be either negative or positive.

To compute the activation volume the barrier energy data versus strain of individual LSEs were used, as shown in Figs. 4.3d, 4.4b and 4.5b. In fact, large data sets involving several hundred LSEs were deployed to obtain the activation volume estimates. Fig. 4.6b shows the distribution of activation volume estimates derived from the evolution of individual LSEs as a function of applied strain. To obtain an estimate of the activation volume, eqn. 4.2 is fitted to each barrier-energy evolution with the constraint that the parameter $E(\tau = 0)$ equals the zero-load barrier energy. Only an estimate of the barrier energies can be obtained, because Figs. 4.3d, 4.4b and 4.5b clearly show a non-linear behaviour which cannot be fitted well to a straight line. For isotropic strain, Fig. 4.6b shows that the activation volume is distributed with a mean of approximately $0.005 \sigma_{11}^3$ – a result that is compatible with the trends seen in Fig. 4.7. The distribution of activation volumes associated with a pure shear geometry is much broader and covers both positive and negative values, with a bias towards the latter — a result that is again compatible with Figs. 4.3 and 4.6a.
Figure 4.6: a) Mean of the barrier energies derived from the ART$n$ data and shown in Figs. 4.3 to 4.5, as a function of their corresponding strain magnitudes. The mean barrier energy for shear is computed by taking the average of the mean barrier energies in XY, YZ and ZX directions. b) Normalised distributions of the estimated activation volume due to pure shear and isotropic loading geometries.

Figure 4.7: Barrier-energy evolution as a function of isotropic stress magnitude (isotropic strain $\times$ bulk modulus) for several individual LSEs derived via a combination of ART$n$ and NEB.
4.4.4 Redundancy in ART\textsuperscript{n} generated saddle-points and usage of NEB/ART\textsuperscript{n} method

Table 4.1 shows the percentage of redundant saddle-points at different loading conditions and compares it with the redundancy percentage of the unloaded state. It is seen that the percentage of redundancy for the loading geometries analysed varies between 4\% and 13\%. There is no clear trend as to whether the redundancy increases or decreases on increasing the shear strain, this is seen by comparing redundancy values at $\gamma = 0$, $\gamma = 0.015$, $\gamma = 0.03$. One trend seen in Table 4.1 is that there is an increase in the percentage of redundant saddle-points correlated with an increase in the number of ART\textsuperscript{n} runs. An obvious question that arises here, is why all the loading geometries are not run with the same number of ART\textsuperscript{n} runs? The reason is that running ART\textsuperscript{n} simulations for a large number of runs (e.g. 20,000) takes a considerable amount of computation time. Therefore, the goal was to obtain maximum information via an optimized run of ART\textsuperscript{n} on different loading geometries, ranging from 5000 to 20,000 runs. The increase in the percentage of redundant saddle-points with the number of ART\textsuperscript{n} runs is consistent with the work of Kallel [47], who carried out large ART\textsuperscript{n} runs to collect data for 100,000 converged saddle-points, and found an 88\% redundancy. The general increase in redundancy percentage with the number of ART\textsuperscript{n} runs might suggest that the number of available distinct saddle points is saturating for a given size of the sample and the chosen parameter values used in the ART\textsuperscript{n} algorithm.

It is important to note that the trends observed in the distributions of activation energies under different loading conditions change little in the presence of redundant saddle-points. The distribution curves with and without redundant saddle-points are statistically similar, and the numerical values of the mean activation energies are shown in Table 4.2. The data show differences that are well within the standard deviations. This reflects that redundant LSEs arise from many different excitations.
Table 4.1: Percentage of redundant saddle-points obtained via ART\(n\) in the XY, YZ, and ZX loading geometries.

<table>
<thead>
<tr>
<th>Loading geometry</th>
<th>no. of ART(n) runs</th>
<th>(\gamma = 0)</th>
<th>(\gamma = 0.015)</th>
<th>(\gamma = 0.03)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XY</td>
<td>10000</td>
<td>–</td>
<td>6.47%</td>
<td>7.24%</td>
</tr>
<tr>
<td>YZ</td>
<td>5000</td>
<td>–</td>
<td>4.92%</td>
<td>4.34%</td>
</tr>
<tr>
<td>ZX</td>
<td>20000</td>
<td>12.83%</td>
<td>11.81%</td>
<td>9.65%</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of the mean activation energies of distributions with and without redundant saddle-points, obtained in the XY, YZ, and ZX directions.

<table>
<thead>
<tr>
<th>Loading geometry</th>
<th>ART(n) runs</th>
<th>(\gamma = 0)</th>
<th>(\gamma = 0.015)</th>
<th>(\gamma = 0.03)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XY (redundancy)</td>
<td>10000</td>
<td>–</td>
<td>10.9452 ±3.53</td>
<td>10.4376 ±3.67</td>
</tr>
<tr>
<td>XY (w/o redundancy)</td>
<td>10000</td>
<td>–</td>
<td>10.7019 ±3.49</td>
<td>10.5799 ±3.65</td>
</tr>
<tr>
<td>YZ (redundancy)</td>
<td>5000</td>
<td>–</td>
<td>11.1219 ±3.48</td>
<td>10.4871 ±3.46</td>
</tr>
<tr>
<td>YZ (w/o redundancy)</td>
<td>5000</td>
<td>–</td>
<td>11.1821 ±3.49</td>
<td>10.5229 ±3.46</td>
</tr>
<tr>
<td>ZX (redundancy)</td>
<td>20000</td>
<td>11.2093 ±3.36</td>
<td>10.9447 ±3.44</td>
<td>10.7748 ±3.63</td>
</tr>
<tr>
<td>ZX (w/o redundancy)</td>
<td>20000</td>
<td>11.6162 ±3.40</td>
<td>11.2904 ±3.46</td>
<td>11.0715 ±3.61</td>
</tr>
</tbody>
</table>

We now briefly discuss the approach that was used to track an LSE during incremental straining. Table 4.3 shows two test cases for the variation of activation energies and eigenvalues for two particular LSEs for the XY loading geometry. The eigenvalue represents the curvature of the PEL, and how it changes is tracked during the NEB plus ART\(n\) runs. Table 4.3 gives an example of an LSE (LSE-A) in which the barrier energy and curvature vary smoothly with strain. However, sometimes an abrupt change in the curvature is seen (LSE-B in table 4.3 – see values given in italics). Atomic visualization is also used to check whether the LSE structure changes abruptly or smoothly with the application of load.
<table>
<thead>
<tr>
<th>Strain value</th>
<th>Activation Energy (LSE-A)</th>
<th>Eigenvalue (LSE-A)</th>
<th>Activation Energy (LSE-B)</th>
<th>Eigenvalue (LSE-B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>15.3559</td>
<td>-10.8212</td>
<td>11.3341</td>
<td>-32.1439</td>
</tr>
<tr>
<td>0.003</td>
<td>15.0440</td>
<td>-11.6465</td>
<td>11.1890</td>
<td>-33.2750</td>
</tr>
<tr>
<td>0.006</td>
<td>15.0605</td>
<td>-12.2127</td>
<td>11.4448</td>
<td>-34.6459</td>
</tr>
<tr>
<td>0.009</td>
<td>14.9920</td>
<td>-12.7152</td>
<td>11.4463</td>
<td>-35.1019</td>
</tr>
<tr>
<td>0.012</td>
<td>14.6354</td>
<td>-17.9506</td>
<td>11.4222</td>
<td>-35.2912</td>
</tr>
<tr>
<td>0.015</td>
<td>14.3298</td>
<td>-17.8756</td>
<td>11.2219</td>
<td>-34.6085</td>
</tr>
<tr>
<td>0.018</td>
<td>14.2358</td>
<td>-17.8009</td>
<td>11.2077</td>
<td>-32.8043</td>
</tr>
<tr>
<td>0.021</td>
<td>14.3802</td>
<td>-17.8225</td>
<td>11.5066</td>
<td>-18.1348</td>
</tr>
<tr>
<td>0.024</td>
<td>14.1158</td>
<td>-17.8138</td>
<td>11.4770</td>
<td>-14.6572</td>
</tr>
<tr>
<td>0.027</td>
<td>14.2082</td>
<td>-17.7836</td>
<td>11.7235</td>
<td>-12.3545</td>
</tr>
<tr>
<td>0.030</td>
<td>14.2929</td>
<td>-17.6771</td>
<td>11.5620</td>
<td>-11.0198</td>
</tr>
</tbody>
</table>

Table 4.3: Variation of activation energies and eigenvalues of two LSEs at incremental shear loading on the XY plane.

### 4.4.5 NEB results of individual LSEs

Table 4.4 shows a parametric study of the MEP of one LSE in the unloaded state. The NEB parameters presented in this table correspond to those of Fig. 4.8. Two results can be seen here. First, there are variations in the MEPs with the number of images used. Secondly, there is a weak sensitivity for the considered range of spring constants. Fig. 4.8 shows a lateral shift when the number of images is lowered. The MEPs seem to converge for varying spring constants when the number of images is higher (in this case 39 images), displaying a more accurate MEP. It is emphasized that only the maximum of these MEPs are used as a starting estimate for the ART algorithm. Overall, there is no great change in the MEP structure on application of external load. What is interesting is that the MEPs often move laterally on incremental shear straining, indicating that the PEL shifts under shear. For the loaded states, trends similar to that in the unloaded state are seen. It is additionally observed that for the MEPs between loaded configurations, small bumps sometimes emerge. In all cases studied in detail, however, their presence did not correspond to an intermediate state,
and could be removed by decreasing the number of images. For shear, and compressive and tensile loading conditions, Figs. 4.9, 4.10 and 4.11 show the MEPs of one LSE (different from that in Fig. 4.8). The expected trends are seen in these MEPs, which are an upward shift in the activation energy axis for compression, and a downward shift for tension. For shear, the MEPs can shift either upwards or downwards with respect to the activation energy. For the particular LSE shown in Fig. 4.9, the MEPs have moved downwards under incremental shear loading. Slight lateral shifts can also be seen in that case.

<table>
<thead>
<tr>
<th>no. of images / spring const</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>A1</td>
<td>B1</td>
<td>C1</td>
</tr>
<tr>
<td>19</td>
<td>A2</td>
<td>B2</td>
<td>C2</td>
</tr>
<tr>
<td>29</td>
<td>A3</td>
<td>B3</td>
<td>C3</td>
</tr>
<tr>
<td>39</td>
<td>A4</td>
<td>B4</td>
<td>C4</td>
</tr>
</tbody>
</table>

Table 4.4: Matrix displaying the legend for Fig. 4.8 at the unloaded state for varying NEB parameters

![Graph showing MEPs](image)

Figure 4.8: Variation of the MEPs of a particular LSE at zero load by variation of the NEB parameters. The figure legend is described in Table 4.4.
Figure 4.9: Variation in the shape of the MEPs under shear loading at different shear strains.

Figure 4.10: Variation in the shape of the MEPs under compressive loading.
4.5 Atomic-scale visualization

A number of LSEs is now considered in detail. To visualize the atomic-scale activity of an LSE as a function of strain and to compare it to the corresponding LSE under zero load, the affine deformation component associated with the applied shear-strain is first subtracted from each configuration. The remaining heterogeneous non-affine component for the initial, activated and final state is then inspected.
Figure 4.12: Minimum energy path of two representative LSEs shown as energy change in going from the initial configuration to the activated and final configurations. Values are shown for the zero-load, XY, YZ, and ZX shear-strain (2 × shear strain = 0.03) configurations.

In what follows, the affine-corrected atomic displacement fields are shown between the initial and activated configurations, and the activated and final configurations. To more clearly identify the atomic motion associated with the corresponding LSE, atomic displacements greater than 0.1σ_{11} are inspected.

Here, two representative LSEs will be investigated, which are labeled as LSE1 and LSE2. Fig. 4.12 displays the corresponding MEPs in terms of only the activated and final-state energy difference for the zero-load and three shear-strained configurations. The MEP associated with LSE1 (Fig. 4.12a) reveals a non-negligible change in barrier energy with all applied shear-strain barrier energies decreasing, demonstrating differing degrees of response of LSE barrier energies to different loading geometries, as reflected in the general changes in the LSE distributions (Fig. 4.3). For LSE2, the associated MEP (Fig. 4.12b) reveals a relative insensitivity to the application of shear-strain, with only the YZ and ZX shear-strain geometries resulting in a noticeable increase in the barrier energy.
Figure 4.13: Atomic displacement fields of two representative local structural excitations (LSEs): a) LSE1 and b) LSE2. Only the largest atomic displacements are shown. For each case, the atomic displacement vector between the initial and activated, and the activated and final configurations is shown, with the colour of the arrows reflecting the loading mode. The coloured balls visualise the position of the initial zero-load configuration. Both LSEs display the common structure of sequential movement of atoms, in which one atom moves approximately a nearest-neighbour distance to replace another atom — see ref. [102]. Graphic visualization is performed using OVITO [103].
Figure 4.14: For the two considered LSEs, i.e., a) LSE1 and b) LSE2, a plot of the cumulative barrier energy versus atomic displacement is constructed by adding the change in local energy of those atoms with an atomic displacement less than the horizontal axis value. The point-colours represent the number of atoms which have contributed thus far to the cumulative barrier energy, and the line colours represent the shear-strain geometries — see the colouring scheme in Figs. 4.12 and 4.13.

To gain some insight into these trends, Fig. 4.13 plots the affine-corrected atomic displacement fields between zero-load and XY, YZ and ZX shear-strain configura-
tions for both LSEs considered. Such displacements are visualized by vectors which point from the initial atom position to the activated atom position, and from the activated one to the final atom position. The balls show the initial atom position of the zero-load configuration and the colour of the displacement vectors indicates the loading geometry. The figures only show the central LSE structure. For both LSEs, a sequence of nearest-neighbour atoms is seen to move a distance of approximately $\sigma_{11}$, demonstrating the string-like structure of LSEs seen in Ref. [102]. That is, atom “1” moves to the approximate position of atom “2”, atom “2” moves to the approximate position of atom “3”, and so on. These atoms, which undergo displacements comparable to $\sigma_{11}$ (which is approximately the mean distance between atoms) constitute the central structure of the LSE. Displacements of $\sim \sigma_{11}$ can occur either mainly between the initial and activated (activated and final) configurations with only negligible displacement between the activated and final (initial and activated) configurations, or involve displacements along the entire trajectory: initial $\rightarrow$ activated $\rightarrow$ final, as is the case for atom “4” in Fig. 4.13a.

Inspection of the central LSE1 structure (Fig. 4.13a) reveals differences with respect to the loading geometry. Indeed, for the YZ and ZX shear-strain configurations, the atom labelled “1” differs from that of the zero-load and XY shear-strain configurations (see lower right-hand inset to Fig. 4.13a). Also, the trajectory of atom “4” (see upper left-hand inset to Fig. 4.13a) is strongly modified by the loading mode where the saddle-point position for the YZ configuration differs from that of the XY and ZX configurations. Trajectories 1 $\rightarrow$ 2, 2 $\rightarrow$ 3, and 5 $\rightarrow$ 6 (atom 6 not shown) are approximately within the YZ plane, whereas trajectory 4 $\rightarrow$ 5 is approximately perpendicular to this plane. It is this latter trajectory that is most affected by the YZ shear-strain (Fig. 4.12a). This suggests that the extent of change in the barrier energy of an LSE under load is related to its orientation with respect to the loading geometry.
For LSE2, inspection of the atomic displacement field (Fig. 4.13b) also reveals a string-like structure where only the ZX shear-strain central structure differs significantly from the zero-load case. This is also the shear-strain geometry for which the barrier energy increases the most (Fig. 4.12b). Here, the combined trajectory $1 \rightarrow 2 \rightarrow 3$ is most affected (see inset to 4.13b), in which the atom position of the activated state within trajectories $1 \rightarrow 2$ and $2 \rightarrow 3$ has changed. For this LSE, the central structure is approximately in the ZX plane, again indicating a correlation between LSE structure, barrier energy change, and loading geometry.

For both LSE1 and LSE2 there exists a less local field of smaller displacements around the central structure (omitted in Fig. 4.13 — see Ref. [102]). This surrounding field of displacements generally describes an outwards expansion of nearby atoms in the activated state, followed by a contraction as the LSE relaxes to its new local minimum (the final state). Inspection of these “accommodating” displacement fields reveals differences in their spatial extent for the three shear-strain loading geometries.

To gain quantitative insight into the origin of the barrier energy with respect to atomic displacement as a function of loading, the change in local atomic energy between the initial and activated configurations is calculated — the sum of which would give the total barrier energy. These local energies are now distinguished in terms of their corresponding atomic displacement magnitudes (between the initial and activated configurations). Fig. 4.14 plots the cumulative barrier energy with respect to increasing displacement magnitude interval. In this figure, the horizontal axis represents an upper atomic displacement magnitude threshold, whereas the vertical axis represents the summed change in energy of these atoms satisfying this threshold — the cumulative barrier energy. The colour of each data point reflects the number of atoms contributing thus far to the cumulative barrier energy. At a large enough displacement threshold, all 1728 atoms will be included and the cumulative barrier energy saturates to the actual barrier energy. As in Fig. 4.12, the colour of the
connecting line reveals the loading geometry.

Fig. 4.12 reveals that those atoms which exhibit very small displacements contribute little to the barrier energy, with their net contribution often being negative. Such atoms are generally distant from the central LSE structure and involve displacement magnitudes typical of the non-affine deformation component ($< 0.1\sigma_{11}$). Most of the atoms within the simulation cell are within this regime of displacement magnitude. Atoms involving displacements comparable to, but larger than, $0.1\sigma_{11}$ tend to contribute positively to the barrier energy. Such atoms are generally in closer proximity to the LSE, mostly surrounding the central structure, and contribute to about half of the total barrier energy. Those (few) central atoms with displacements in the regime of $> 0.5\sigma_{11}$ contribute to the remaining cumulative barrier energy. In the case of LSE1 (Fig. 4.14a), this contribution may either be positive or negative, whereas for LSE2 (Fig. 4.14b), it is only positive.

A number of other LSEs were investigated in a similar manner, with particular emphasis on those with a low barrier energy. The central structure of such LSEs is also found to involve several atoms whose collective motion is chain-like. This is compatible with past ARTn work, which found little correlation between atom number and barrier energy [102]. In general, similar qualitative trends were seen, with the central atomic LSE structure sometimes differing according to the shear-strain geometry with either an increase or decrease in the corresponding barrier energy.

4.6 Discussion

The main findings in this chapter are that upon an isotropic compression/tensile loading, the LSE barrier energies increase/decrease, leading to a general shift of the LSE barrier-energy distribution; and that application of a pure shear-strain generates a general broadening of the LSE barrier energy distribution. Atomic visualization of particular LSEs under load suggests that their orientation with respect to the loading
geometry may play a role in how the corresponding barrier energy is modified with respect to load. This latter result is at best qualitative and motivates the question of what quantitative features of a particular LSE, under zero-loading conditions, influence the response of its barrier energy to an applied load.

One such signature might be the change in internal stress between the initial and activated configuration of an LSE, calculated under zero load. Fig. 4.15a displays a scatter plot of such a change in stress as a function of barrier energy, in which the hydrostatic pressure and the shear stresses are shown. These quantities have been calculated using a local version of eqn. 3.2, which gives the local atomic stress tensor for each atom (see Ref. [102]). Inspection of the shear stresses show little correlation with barrier energy, a trend first noticed by Rodney and Schuh [45]. On the other hand, Fig. 4.15a shows a very clear linear correlation between barrier energy and the change in hydrostatic pressure (the red points in the figure). It is noted that the observed approximate linear trend of barrier energy with change in hydrostatic pressure, and the lack of correlation with the shear components, does not result in the quadratic relation between von Mises shear and barrier energy seen in Refs. [51, 52]. However, the quadratic trend seen in Refs. [51, 52] is for the low-end barrier-energy regime and for barrier-energy distributions which do not tend to zero with zero barrier energy, reflecting the fact that the atomic configurations in those works are (by design) less relaxed than the atomic configurations studied in this thesis.
Figure 4.15: a) Scatter plot of change in internal stress between the zero-load initial and activated configurations versus barrier energy, and b) scatter plot of change in internal shear stress between the zero-load initial and activated configurations versus the change in barrier energy as a result of an imposed XY shear-strain.

The results of Fig. 4.15a provide an immediate understanding of why the barrier energy increases for a compressive load and decreases for a tensile load (see also Figs. 4.4 and 4.5). Indeed, it reflects the very general result that the saddle-point configuration will always involve an expansion of the surrounding lattice to accommodate the central migrating atomic structure, which is itself in a compressive environment. In fact, approximately half of the hydrostatic pressure signature results from the surrounding lattice (here defined as displacement magnitudes comparable to $0.1\sigma_{11}$), while the remainder originates directly from the central structure of the LSE. Thus, under tension/compression the energy required for such an accommodation will be reduced/increased, resulting in a decrease/increase in the barrier energy.

Fig. 4.15b plots the three shear-stress components as a function of the actual change in barrier energy of the corresponding LSE, for the case of an externally applied XY shear-strain (at a shear-strain magnitude of 0.03). For the case of the internal XY shear signature of the zero-load LSE, a linear correlation with the change in barrier
energy becomes evident, whereas no such correlations are seen for the YZ and ZX internal shear stresses. Again, the correlation originates from both the central LSE structure and the surrounding matrix. As in the case of isotropic strain, this result facilitates an understanding of the shear-strain-dependent results shown in Fig. 4.3. That is, a particular LSE will have, e.g., a positive XY shear-stress component, and an applied shear-strain (which results in a negative XY shear stress) will reduce the barrier energy — or vice versa. Given that there should be no particular bias regarding the “orientation” of an LSE under zero load, application of pure shear-strain should only result in a broadening of the barrier-energy distribution. However, the fact that Figs. 4.3 and 4.6a demonstrate a small reduction in the average barrier energy with respect to an applied shear-strain does suggest a more complex stress signature involving the hydrostatic stress component.
Chapter 5

Summary and outlook

In this thesis work, unit plastic events underlying macroscopic plasticity in BMGs were studied at zero and non-zero applied load. One very clear result is that LSEs can occur everywhere, with only a weak correlation between their spatial position and the local structural environment. Important findings are that a) most LSEs consist of many small atoms; and b) low barrier energy corresponds to negative or low Kelvin eigenshear moduli. Because the LSEs considered are directly linked to their initial and final states (no intermediate local energy minimum needs to exist), the ARTn-obtained LSEs might be identified using well-known \( \beta \) structural transformations. However, this must be further investigated by looking at multiple LSE activities and the possible identification of \( \alpha \) structural transformations. The central atomic structure of the LSEs are found to have a string-like geometry in which one atom replaces another neighbouring atom. Such structures appear different from the early free volume model suggested by Spaepen [23], where a thermally activated structural excitation involved a single atomic migration towards a region of free volume. However, it is interesting to note that the string-like structures seen in this thesis work do occur in the vicinity of free volume regions. In future work, it is proposed to
investigate where these string-like LSEs end up, and whether they migrate directly towards free volume regions.

This thesis investigated how the potential energy landscape of a model binary Lennard-Jones glass system is modified upon application of an external stress. In particular, how the barrier-energy distribution of local structural excitations (LSEs) changes. It was found that for isotropic compressive or tensile strain (i.e. volume change) the barrier-energy distribution shifts to higher and lower barrier energies, respectively. On the other hand, the application of pure shear-strain results in a dominant broadening of the distribution. Microscopic barrier-energy information as a function of loading provides quantitative insight into the energy landscape of the \( \beta \) processes facilitating the \( \alpha \) processes responsible for macroscopic plasticity in amorphous solids, and will hopefully aid in the development of macroscopic deformation models based on a microscopic thermal activation picture.

The unit plastic events seen in this thesis also appear to be structurally different from the shear transformations (ST) proposed in the early thermal activation model of Argon [3]. What is interesting, however, is the fact that for these string-like structures the internal hydrostatic pressure of the LSEs correlates linearly with their activation energies – see Fig. 4.15 in chapter 4. This reflects the fact that the saddle-point configuration will always involve an expansion of the surrounding lattice to accommodate the central migrating atomic structure, which is itself in a compressive environment. In fact, approximately half of the hydrostatic pressure signature results from the surrounding lattice while the remainder originates directly from the central structure of the LSE. Thus, under tension/compression, the energy required for such an accommodation will be reduced/increased, resulting in a decrease/increase in the barrier energy. This is precisely the picture first proposed by Argon, in which there is a change in elastic energy partly within and outside of the central structure, associated with the local expansion of the LSE. Thus the LSEs presented involve aspects of the
early pictures developed by both Argon and Spaepen [3, 23]. In fact, the change in
barrier energy correlates strongly with the LSEs’ shear-stress signature in the loading
mode (see Fig. 4.15 in chapter 4), indicating that the string-like structures have
a clear shear-stress signature. Future work should include a detailed study of the
characteristic stress signatures of the activated state – an aspect that could not be
performed using the small samples considered in the present work.

The activation volumes obtained in this thesis represent only a small fraction of
an atomic volume, which is considerably smaller than what is normally seen in exper-
iments. Indeed, experiments can give values that are typically several (or several tens
of) atomic volumes (see for example ref. [18]). Two aspects need to be considered
when comparing activation volumes derived here to those extracted from experiments.
Firstly, experiments generally probe macroscopic plasticity, which at low enough tem-
peratures involves the nucleation, propagation and arrest of shear bands [22]. The
activation volumes here represent those of individual LSEs — structural transitions
that have in the past been identified as $\beta$ transitions [102] — whereas macroscopic
plasticity is generally believed to be mediated by $\alpha$ transitions (which are facilitated
by multiple $\beta$ activity). Secondly, such activation volumes are usually derived by
assuming a single barrier energy, which is expected to have a non-trivial temperature
and stress dependence arising from both the thermal accessibility and stress depen-
dence of the underlying barrier-energy distribution. Thus the connection between an
LSE’s individual activation volume and that probed by experiment is not obvious.

A pertinent question that may be asked here is why this thesis investigated barriers
in three loading geometries (XY, YZ, ZX) when glass is known to be isotropic? While
it is true that glass is isotropic at the macroscopic length scale, this may not hold true
at the microscopic length scale, where heterogeneities are seen. In fact, as the results
in chapter 4 suggest, the LSE structures can be different under the three loading
geometries – as seen by atomic visualization. This is the reason why the distributions
of barriers were computed under the XY, YZ and ZX loading geometries. However, no significant statistical differences were seen in the three LSE distributions, indicating isotropy above a certain length scale less than that of the simulation cell used, where atomic level heterogeneities average out. Another reason for investigating the LSEs under three loading geometries was to establish the hypothesis proposed in [60], which suggested that the barrier energy of an LSE decreases when the loading is compatible to LSE deformation, implying that the corresponding stress component is hindered. Thus the idea to further investigate the correlations between the stress components and the barrier energy was conceived, which led to the detailed discussion in chapter 4.

In all the results obtained via ART\(n\) in this thesis, it is important to note that only the tail of the barrier energy distribution, which represents the low energy barriers, is physically relevant. Hence, it could be asked why this thesis studies the full distribution. Assuming that the number of barriers scales exponentially with the system size [60], larger system sizes would make it more likely that high barriers are overcome. Thus there is the possibility of a rare occurrence of LSEs with energy barriers corresponding to the mean of the total distribution. However, the highest energy barriers which ART\(n\) finds are physically irrelevant and such LSEs in most likelihood will never occur due to the difficulty associated with traversing a barrier of the order of \(25 \epsilon\), where the thermal energy scale of the Lennard-Jones system is of the order of \(\epsilon\).

Based on the findings of this thesis, an immediate future research direction that is envisaged is the traversal of an \(\alpha\)-structure via collective \(\beta\)-activity. The traversal of an \(\alpha\)-structure can be subdivided into two phases: one is the ascent until a high enough saddle point is reached, and the second is the descent from the highest saddle-point in the \(\alpha\)-structure to a deep minimum. Both the ascent and the descent phases involve traversals of many \(\beta\)-structures (or LSEs). Each of these \(\beta\)-structures can be
traversed via first employing the ARTn technique to converge onto a saddle-point and subsequent molecular statics relaxations for the system to end up at a local minimum that differs from the initial minimum. From the new local minimum, which is often denoted as the final state with respect to a $\beta$-structure, ARTn can be run again to obtain a distribution of the neighbouring saddle-points. This new distribution of $\beta$-structures can be constructed which is available to be traversed via ARTn. Such an iterative procedure can be followed to climb up the $\alpha$-hill.

There can be different strategies for traversing the $\alpha$-structures. Due to the fact that only the low energy barriers are the physically relevant transitions, this thesis recommends employing these $\beta$-structures to facilitate the journey of the system out of the mega-basin. From the saddle-points obtained via ARTn, the LSE corresponding to the lowest barrier height is selected and its corresponding final state computed. From that final state, ARTn is run again and the procedure is repeated until a high enough saddle-point is reached. It may be argued here that the LSE corresponding to the lowest difference in the energy between the final state and the initial state should be considered rather than the LSE corresponding to the lowest barrier energy. However, in this thesis, it is found that there is a linear correlation between the barrier heights and the energy differences between the final and the initial states, suggesting that the low barrier LSEs correspond to low differences in the energy between the final and the initial states (see chapter 3). It is for this reason that the final state energy does not need to be considered as a criterion for climbing the $\alpha$-structure, because necessary information can be gained from the saddle-point energy without having to relax the distribution of saddle-points to obtain their corresponding final state minima. The work of [48] demonstrates that the prefactor also has to be considered when choosing the next LSE. Thus rather than using the energy barrier criterion, the individual transition rate could be used, as in the work of [45], which combined ARTn with kinetic Monte Carlo simulations. The resulting $\alpha$-structure is envisaged
to undertake a complex structural change (when compared to the starting state). Therefore, the descent phase will need to be carefully constructed, by traversing each intermittent \(\beta\)-structure step-by-step using a combination of ARTn and subsequent molecular statics steps. The descent phase can be expedited via a direct quench with molecular dynamics. The above procedure, in which one can effectively choose the path through the PEL between the potential energy valley, may allow for investigations of how the \(\alpha\)-landscape behaves as a function of different types of \(\beta\)-activity, i.e., whether it is spatially localized or scattered throughout the simulation cell. How an applied load will bias such statistics should also be investigated.

It is imperative to discuss here how the results obtained from ARTn fall in the context of \(\beta\)- and \(\alpha\)-structures. In this thesis, it is assumed that ARTn primarily probes \(\beta\)-structures. However, this is still not clear, given the observation that, if the system is relaxed when it is outside the basin of attraction of the initial minimum, it may not fall back into the initial state. This suggests that ARTn may identify multiple \(\beta\)-structures which are part of a larger \(\alpha\)-structure and not necessarily just one elementary \(\beta\)-transition. Detailed investigation to clarify this picture is recommended as future work.

The physically relevant barriers are the low-energy barriers. Methods other than ARTn may also be employed to investigate these barriers and how they perform. The performance of dynamical methods mentioned in chapter 1 when applied to low-energy barriers have been discussed in [53]. It is stated in that study that the boost which the accelerated dynamical methods provide is reduced for low-energy barriers. This is the case for hyperdynamics, temperature-accelerated dynamical methods and in some cases for parallel-replica dynamics methods. Thus the efficiency of these dynamical methods is poor when applied to low-energy barriers. In the hyperdynamics method, the boost can be enhanced by selecting a larger bias, which, however, has the consequence that all the low-energy barriers will be blocked, destroying low-energy
barrier physics and thus rendering this approach unsuitable for studying physically relevant LSEs. Their usage may thus not be recommended for extended PEL exploration. In the metadynamics method [54], the adaptive bias needs to be chosen such that the system does not fall back into an old minimum and that it is still low enough to capture physically relevant energy barriers. A proper choice of the bias potential is therefore of paramount importance while applying metadynamics to study low-energy barriers for climbing up an $\alpha$-structure. Development of advanced bias potentials that are low enough to capture the physically relevant barriers and are at the same time capable of pulling the system out of the local minimum quickly, while maintaining the correct state-to-state transition, is necessary, if metadynamics is to be employed for extended PEL exploration.

Lastly, the author notes that some of the larger samples prepared for this thesis could not be tested, because the thesis focus was primarily to obtain a qualitative picture of correlations of the LSE structure- and energy-scales with the local atomic environment, with and without application of an external load. For future work, the author recommends applying for dedicated computational time at the CSCS supercomputing centre in Lugano to test some of these samples. Deploying these larger samples and/or using more realistic model potentials would be a step towards gaining quantitative insight into the atomic-scale features which may bring the findings of this thesis closer to the experimental stage. However, the use of more realistic inter-atomic multi-component potentials is not expected to fundamentally change the current results, although some additional details of the LSE structure, unique to the corresponding potential/system, are expected to occur which are not present in the LJ model system studied here.
CURRICULUM VITAE

Personal details

Name: Soumya Swayamjyoti
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Education

- **Doctoral studies** (2012 – 2016) in the field of “Bulk Metallic Glasses” in a collaborative arrangement between the Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich and the Condensed Matter Theory group, Paul Scherrer Institute, Switzerland,

  *Thesis: Atomistic simulations to study metallic glasses: a microscopic investigation of local structural excitations.*

- **Master of Science** in “Computational Mechanics of Materials and Structures” (10/2009 – 4/2012), from University of Stuttgart, Germany (with one semester of studies at UPC Barcelona),

  *Thesis: Finite element implementation of orbital-free density functional theory.*

- **Bachelor of Technology** in “Civil Engineering” (2004 – 2008), from National Institute of Technology Karnataka, Surathkal, India,


Journal papers (refereed)


**Honors and awards**

• **Erasmus Mundus scholarship**, a full scholarship by the European Commission for Master studies. 10 to 15 full scholarships are awarded in computational mechanics every year to candidates selected from a pool of applicants from all over the world. The selection consortium comprises of University of Stuttgart in Germany; International Center for Numerical Methods in Engineering (CIMNE) at Technical University of Catalunya (UPC) Barcelona in Spain; Ecole Centrale Nantes in France; and Swansea University in United Kingdom.

• Passed the All India Engineering Entrance Examination (2004), which is a nationwide examination in Mathematics, Physics and Chemistry to gain admission for undergraduate studies at the National Institute of Technology (NIT) Karnataka, which is an institute of national importance by the NIT act of the Indian parliament.

• Zonal rank 12 in Regional Mathematics Olympiad (RMO), and represented the zone in Indian National Mathematics Olympiad (INMO). \( \sim \) 500 students were selected to participate in the INMO after nationwide selections at zonal levels.
Conferences and workshops


Seminar talks

- ‘Microscopic structural excitations in model glass systems under zero and applied load’, group seminar, 17.10.2014, Laboratory of Metal Physics and Technology, ETH Zurich, Switzerland.

- ‘Local structural excitations in model glasses’, group seminar, 11.11.2013, Laboratory of Metal Physics and Technology, ETH Zurich, Switzerland.

- ‘Atomistic modeling of structural glasses’, group seminar, 12.11.2012, Laboratory of Metal Physics and Technology, ETH Zurich, Switzerland.
Graduate level coursework

- Micromechanics of materials and homogenization methods
- Atomistic modelling of materials
- Theory and numerics of materials at large strains
- Foundations of single and multiphasic materials
- Continuum mechanics
- Finite element methods
- Boundary element methods in statics and dynamics
- Programming for engineers and scientists
- Numerical methods for partial differential equations
- Computer modelling
- Advanced fluid mechanics

Term projects and summer internships

- Molecular dynamics simulations with LAMMPS (Master studies, University of Stuttgart)
- Extreme loading of aircraft fan blade (Master studies, UPC Barcelona)
- Theory of plates and hyperboloid structures (Undergraduate studies, NIT Karnataka)
- An experimental investigation of ground-water quality in south-west India (published in NITK research bulletin)
• DSMC analysis of argon flow over a cylinder (summer internship, IIT Kanpur)

• Shock capturing for hypersonic flows (summer internship, IIT Delhi)

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• Laboratory of Metal Physics and Technology, ETH Zurich

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• Institute of Applied Mechanics (Chair of Materials Theory), University of Stuttgart

• Laboratory of Computational Methods and Numerical Analysis, UPC Barcelona

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Bibliography


