Local excitations in amorphous solids

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Two things awe me most, the starry sky above me and the moral law within me.

— Immanuel Kant
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Abstract

Amorphous solids are structurally disordered. They are very common and examples include glasses, colloids, and granular materials. However, they are far less understood than crystalline solids. For amorphous solids key aspects of these materials are controlled by the presence of excitations in which a group of particles rearranges. This motion can be triggered by either: (a) quantum fluctuations associated with two-level systems (TLS) that dominate the low temperature properties of conventional glasses and have practical importance on superconducting qubits; (b) thermal fluctuations associated with activations that are related to the famous and challenging “glass transition” problem; (c) exerting an external stress or strain associated with shear transformations that control plasticity. It is thus important to understand how temperature and system preparation determine the density and geometry of these excitations. The possible unification of these excitations into a common description is also a fundamental problem.

All these local excitations are thought to have a close relationship with Quasi-localised modes (QLMs), local normal modes of the Hessian (Stiffness Matrix), that are present in the low-frequency vibrational spectrum of amorphous solids. To study the local excitations we thus proceed by understanding the properties of QLMs and clarifying their relation to the local excitations.

In this thesis: (1) we provide a theory for the density of QLMs, $D_L(\omega) \sim \omega^\alpha$, that establishes the link between QLMs and shear transformations for systems under athermal quasi-static loading. It predicts two regimes depending on the density of shear transformations $P(x) \sim x^\theta$ (with $x$ the additional stress needed to trigger a shear transformation). If $\theta > 1/4$, $\alpha = 4$ and a finite fraction of quasi-localised modes form shear transformations whose amplitudes vanish at low frequencies. If $\theta < 1/4$, $\alpha = 3 + 4\theta$ and all QLMs form shear transformations with a finite amplitude at vanishing frequencies. We confirm our predictions numerically.

(2) We present a protocol to generate extremely stable computer glasses at minimal computational cost. It consists of an instantaneous quench in an augmented potential energy landscape, with particle radii as additional degrees of freedom (i.e. we use ‘breathing’ particles). Strikingly, we find that the density of QLMs displays a gap in our most stable computer glasses which is consistent with the lack of plasticity we observe at small stress.

(3) We propose a unification of theories predicting a gap in the spectrum of QLMs that grows upon cooling, with others that predict a pseudo-gap $D_L(\omega) \sim \omega^{\alpha}$. Specifically, we generate glassy configurations of controlled gap magnitude $\omega_c$ at zero temperature ($T=0$), using our ‘breathing’ particles, and study how such gapped states respond to thermal fluctuations.
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We find that (i) the gap always fills up at finite $T$ with $D_L(\omega) \approx A_4(T)\omega^4$ and $A_4 \sim \exp(-E_a/T)$ at low $T$, (ii) $E_a$ rapidly grows with $\omega_c$, in reasonable agreement with a simple scaling prediction $E_a \sim \omega_c^4$ and (iii) at larger $\omega_c$ excitations involve fewer particles, as we rationalise, and eventually become string-like. Following these observations, we propose an interpretation of mean-field theories of the glass transition, in which the modes beyond the gap act as an excitation reservoir, from which a pseudo-gap distribution is populated with its magnitude rapidly decreasing at lower $T$. We discuss how this picture unifies the rarefaction as well as the decreasing size of excitations upon cooling, together with a string-like relaxation occurring near the glass transition.

(4) Preliminary results on the local excitations are presented for glasses (realistically prepared glasses) obtained by an instantaneous regular quench from equilibrated configurations at low temperature $T_p$ obtained by the SWAP Monte Carlo method. We find that in these glasses, (i) rearrangements become string-like when the glass becomes more stable. (ii) For small $T_p$, a slow annealing does not affect $A_4$. This indicates that the reservoir effect is not the dominant one controlling $A_4$. (iii) One local rearrangement can be associated with several QLMs. (iv) We test the idea that these soft regions are induced by rare fluctuations of key quantities controlling stability, such as coordination and pressure.

(5) I argue that TLS are dominated by nearly symmetric DWPs with a characteristic frequency $\omega_0$. It leads to that the density of TLS, $n_0$, is proportional to $A_4$ and to the fraction $f_{\omega_0}$ of double-wells at $\omega_0$. Based on this relation, I estimate $n_0$ in glasses prepared from different temperature $T_p$ obtained by the SWAP Monte Carlo method. I find that $n_0$ decreases by a factor of 300 in ultrastable glasses than poorly prepared glasses with both $A_4$ and $f_{\omega_0}$ playing a significant role. More significantly, the estimations of $n_0$ are consistent with the order of magnitude of the change in $n_0$ found in amorphous silicon.

Keywords: Amorphous solids, local excitations, two-level systems, shear transformations, quasi-localised modes.
Abstract
Les solides amorphes sont structurellement désordonnés. Ces systèmes sont omniprésents autour de nous, et incluent notamment les verres, les colloïdes, et les matériaux granulaires. Leurs propriétés sont cependant bien moins comprises que celles des solides cristallins. Pour les solides amorphes, des aspects clés de ces matériaux sont contrôlés par la présence d’excitations qui amènent des groupes de particules à se réarranger localement. Ces réarrangements peuvent être déclenchés soit (a) par des fluctuations quantiques associées à l’existence de systèmes à deux niveaux ("two-level systems" ou TLSs), qui dominent les propriétés à basses température des verres dit "conventionnels", et ont des conséquences pratiques importantes, notamment pour les cubits supraconducteurs; (b) par des fluctuations thermiques associées à des processus d’activation reliés au fameux problème de la “transition vitreuse”, qui demeure un challenge à ce jour; (c) par une contrainte ou déformation externe, associée à des transformations sous cisaillement ("shear transformations") qui contrôlent la plasticité de ces matériaux. Il est par conséquent important de comprendre comment la température et les protocoles de préparation d’un système donné déterminent la géométrie de ces excitations. Une autre question fondamentale est la possible unification de ces excitations en une description commune.

Toutes ces excitations locales sont considérées comme étant intimement reliées aux modes quasilocalisés ("quasi-localised modes" ou QLMs), qui sont les modes normaux locaux de la matrice hessienne (i.e. le tenseur de rigidité) qui sont présents dans les bases fréquences du spectre vibrationnel des solides amorphes. Afin d’étudier les excitations locales, notre approche consiste ainsi à d’abord comprendre les propriétés des QLMs, puis de clarifier leur relations aux excitations locales.

Dans cette thèse : (1) Nous proposons une théorie pour la densité des QLMs, $D_L(\omega) \sim \omega^\alpha$, qui établit un lien entre les QLMs et les des transformations sous cisaillement ("shear transformations") pour des systèmes athermiques sous une déformation quasistatique. Cette théorie prédit l’existence de deux régimes pour la densité de ces transformations $P(x) \sim x^\theta$ (où $x$ correspond à la contrainte additionnelle nécessaire pour déclencher une telle transformation). Si $\theta > 1/4$, $\alpha = 4$ et une portion finie des modes quasilocalisés sont associés à des transformations dont l’amplitude tend vers zéro aux basses fréquences. Si $\theta < 1/4$, $\alpha = 3 + 4\theta$ et tous les modes quasilocalisés sont associés à des transformations dont l’amplitude reste finie même dans la limite de fréquence nulle. Nous confirmons ces prédictions numériquement.

(2) Nous présentons un protocole qui permet de générer numériquement des verres extrêmement stables avec un coût computationnel minimal. Ce protocole consiste à figer
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instantanément les configuration dans un paysage d’énergie potentiel augmenté, qui inclut comme des degrés de liberté additionnels les rayons des particules (i.e. nous utilisons des particules qui “respirent”). De façon remarquable, nous trouvons que la densité de modes quasilocalisés présente un gap, pour les configurations correspondant aux verres les plus stables, ce qui est cohérent par rapport à l’absence de plasticité observée pour des contraintes faibles.

(3) Nous proposons une unification des différentes théories qui proposent d’un part un gap dans le spectre des modes quasilocalisés, gap qui grandit à mesure que l’on explore des températures plus basses, et d’autre part l’existence d’un pseudo gap $D_L(\omega) \sim \omega^\alpha$. Plus spécifiquement, nous générions des configurations de verres avec un gap dont nous pouvons contrôler l’amplitude $\omega_c$ à température nulle ($T = 0$), à l’aide de nos particules qui “respirent”; nous étudions comment ces états avec un gap évoluent en présence de fluctuations thermiques. Nous trouvons que (i) le gap finit toujours par être comblé à une température $T$ finie, avec une densité $D_L(\omega) \approx A_4(T)\omega^4$ et une amplitude $A_4 \sim \exp(-E_a/T)$ à basse température $T$, (ii) $E_a$ grandit rapidement en fonction $\omega_c$, avec un accord raisonnable par rapport à une prédiction de scaling $E_a \sim \omega_c^4$ et (iii) à de plus grandes valeurs du gap $\omega_c$, les réarrangements impliquent de moins en moins de particules (ce que nous sommes à même d’expliquer), et prennent ultimement la forme de petites chaînes. Sur la base de ces observations, nous proposons une interprétation des théories en champ moyen de la transition vitreuse; selon cette interprétation, les modes au-delà du gap constituent un réservoir d’excitations, qui viennent peupler la densité des modes en-dessous du gap par activation thermique, générant une distribution de type pseudo-gap dont l’amplitude diminue très rapidement lorsque la température $T$ décroît. Nous discutons également comment cette interprétation physique permet d’unifier les observations de raréfaction des excitations et de leur taille décroissante, lorsque la température décroît, ainsi que la relaxation sous forme de petites chaînes qui a lieu à proximité de la transition vitreuse.

(4) Nous présentons des résultats préliminaires sur les excitations locales pour des verres préparés de façon plus réaliste. Ceux-ci sont obtenus en figeant instantanément (‘regular quench’) des configurations initialement équilibrées à de basses températures $T_p$ à l’aide d’une méthode de Monte Carlo de type SWAP. Nous trouvons que dans ces verres (i) les réarrangements prennent la forme de petites chaînes lorsque le verre devient plus stable. (ii) Pour de basses $T_p$, une recuison lente n’affecte pas $A_4$. Cela indique que l’effet de réservoir n’est pas celui qui domine le contrôle de $A_4$. (iii) Un réarrangement local peut être associé à plusieurs modes quasilocalisés. (iv) Nous testons l’idée selon laquelle des régions moins rigides (plus ‘soft’) sont générées par de rares fluctuations de quantités clés dans le contrôle de la stabilité, telles que la coordination et la pression.

(5) J’argumente que les TLS sont dominés par des potentiels en double puits (“double well potentials” ou DWPs) quasi-symétriques, avec une fréquence caractéristique $\omega_0$. Cela implique que la densité des TLS, $n_0$, est proportionnelle à $A_4$ et à la fraction $f_{\omega_0}$ de ces double puits à $\omega_0$. Sur la base de cette relation, je détermine une estimation de $n_0$ dans des verres préparés à différentes températures $T_p$ à l’aide d’une méthode de Monte Carlo de type SWAP. J’obtiens que $n_0$ décroit d’un facteur 300 dans des verres ultrastables par rapport à des verres
beaucoup moins stables, avec $A_4$ et $f_{\omega_0}$ jouant un rôle prépondérant. De façon plus significative, ces estimations de $n_0$ sont compatibles avec l’ordre de grandeur du changement de $n_0$ observé dans des matériaux amorphes à base de silicium.

**Mots-clés :** Solides amorphes, excitations locales, états à deux niveaux, transformations sous cisaillements, modes quasi-localisés.
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Introduction

In the last century, much progress has been made towards understanding crystalline solids whose atoms are periodically arranged, resulting in well established theories of their statics, dynamics, thermodynamical properties.

Amorphous solids, which are structurally disordered, are far less understood even though they are also very common in our daily life. Examples of amorphous solids include glasses, colloids, and granular materials [1]. Due to the structural disorder, the energy landscape is filled with many metastable states. Consequently, the system can reside in non-equilibrium states whose properties change over time. Therefore, physical properties of amorphous solids strongly depend on the preparation protocol [2, 3, 4]. For instance, their brittleness, relaxation times and specific heat can be very different for different preparations [5, 6, 7].

Due to the complexities presented by disorder and by the absence of equilibrium, we do not have a unified description in amorphous solids.

0.1 Local excitations in amorphous solids

Key feature of amorphous solid is that they present local excitations where a group of particles can rearrange locally between two metastable states. These local excitations (rearrangements) can be triggered by (i) quantum fluctuations associated with two-level systems (TLS), (ii) thermal fluctuations associated with activations, or by (iii) mechanically exerting an external stress or strain associated with shear transformations.

(i) Two-level systems (TLS)

In crystals, low temperature thermal properties are determined by phonons (quantized plane waves). Both their specific heat and thermal conductivity in three dimensions (3D), are cubic in temperature $T$ which is well explained by the Debye theory. Surprisingly, in the early 1970s, Zeller and Pohl [8] found that the specific heat is approximately linear in $T$ and thermal conductivity is approximately proportional to $T^2$ below 1 Kelvin in amorphous silica, a kind of insulating glassy materials. (See Fig. 1)
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Figure 1 – The experimental measurement of specific heat (a) and thermal conductivity (b) in amorphous and crystalline silica SiO$_2$ plotted in log-log scale with red and blue lines as guidance below 1 K, respectively. Plots are adapted from [8].

Soon after this finding, Phillips [9] and Anderson, Halperin, and Varma [10] independently proposed phenomenological models called the “tunneling two-level systems (TLS)” model to explain these anomalies. The main idea is that an atom or a group of atoms can tunnel between two nearby energy minima in glass at low temperature shown schematically in Fig. 2. The corresponding splitting energy is $E$ given by the WKB approximation: $E = \sqrt{(\delta e)^2 + \Delta_0^2}$ [9, 10], where $\delta e$ is the energy asymmetry and $\Delta_0 \propto \exp(-\tilde{\lambda})$ the quantum tunnelling contribution. By assuming a wide distribution of $\delta e$ and tunnelling matrix element $\tilde{\lambda}$ which depends on the energy barrier $V$, they obtain the density of TLS $n(E = 0) = n_0$ which remains finite. It leads them to obtain the linear specific heat at low $T$. Further, by considering the interaction between TLS and phonons, they explained the quadratic temperature dependence of thermal conductivity.

Due to the successful explanation of thermal anomalies at that time, TLS are believed to be the source to dominate the low temperature properties in insulating glasses *.

*Electrons contribute nothing to their thermal transport.
0.1. Local excitations in amorphous solids

Figure 2 – The sketch of TLS in energy-coordinate space and the corresponding configurations (blue particles). A group of atoms locally rearranges from the left configuration (light blue) to the right configuration (dark blue). The red arrows indicate the displacement field whose direction is also called the reaction coordinate. In energy space, a double well potential is formed along the reaction coordinate, whereby $U$ is the interaction potential, $\delta \epsilon$ is the energy asymmetry, and $V$ is the energy barrier.

Surprisingly, these glasses, despite of the diversity of chemical compositions and structures, present a near universality in $n_0$ below $1K$ \cite{4}. This observation is not readily explained by the “tunnelling TLS” model \cite{11}. The nature of TLS and role of their interactions, specifically towards the formation of a pseudo-gap in the density in these systems is still widely debated on \cite{11, 15, 16, 17}.

TLS are furthermore of practical importance because they cause decoherence in superconducting qubits \cite{18, 19} which are a promising candidate for the construction of a quantum computer. Therefore, reducing the density of TLS becomes an applicational necessity.

Depletion of TLS in ultrastable glass— Several years ago, Ramos et al. \cite{7} and Hellman et al. \cite{20} found experimentally that the specific heat at low temperature is proportional to $T^3$ rather than $T$ in vapour-deposited glasses \footnote{Specifically, $n_0 = \frac{2}{\pi g} Q^{-1}$ where $g$ is the coefficient of the dipole interaction between TLS through elastic medium \cite{11, 12} and $Q^{-1}$ is the internal friction of order $10^{-3}$ \cite{13, 14}.
}. This result implies that the density of TLS, $n_0$, is almost depleted which is in contrast with the previous believe that TLS are always dominant at low temperature and thus shows that their density is not universal after all. Fig. 3 shows that the specific heat in ultrastable glasses (USG) is proportional to $T^3$ at low temperatures distinct from that in conventional glasses. The question of how exactly does system preparation affect the density of TLS remains an open problem.

\footnote{This “tunnelling TLS” model does not quantitatively explain the universality in $n_0$ or $Q$.

\footnote{Note that phonons always contribute to specific heat with $T^3$ term in glass, but this term is much smaller than the TLS’ contribution below $1K$ in a conventional glass where specific heat is linear in $T$.}
Figure 3 – The specific heat divided by $T^3$ varies as a function of $T$ in different glasses, from ref. [7]. "USG" stands for ultrastable glasses whose curves are quite flat at low $T$. It indicates that the density of TLS is significantly lowered.

(ii) Activations

At higher temperatures, $k_B T$ comparable or higher than the local energy barrier, local rearrangements are dominated by thermal fluctuations, namely activations [3, 21, 16] in which a group of particles get over the potential barrier and reach another energy minimum. With increase in the temperature the duration for each activation decreases [21], and eventually the system starts flowing on experimental time scales. This corresponds to the “glass transition” [2, 3, 22]. Experimentally, the glass transition is denoted by a temperature $T_g$ at which the viscosity is of order $10^{12}$ Pa.s and the typical relaxation time $\tau_a$ is of order 100 s [22].

In fragile liquid where $\tau_a$ is super-Arrhenius dependent [22], a decrease in temperature (called $\alpha$ relaxation process), results in an increase of its activation energy and shear modulus [23], which suggests that the energy landscape evolves when cooling. Along this view, it is found that thermally activated events are more and more string-like upon cooling near $T_g$ [24, 25]. The question then begs what controls the geometry of these relaxation events?

(iii) Shear transformations

For glasses below $T_g$ and for granular materials (whose particles’ sizes and masses are quite big so that their thermal fluctuations can be neglected even at room temperature), local rearrangements can be triggered by external shear stress or strain. Such local rearrangements are called shear transformations [26, 27, 28, 29, 30] (see the sketch of a shear transformation process in Fig. 4). Shear transformations control the plasticity of amorphous solids that determines brittleness and the response under external loading, which in turn causes fractures.

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\*Most of time the system vibrates around a minimum and occasionally jumps between different minima.

\*The energy is extracted from the super-Arrhenius dependence [3].
0.2. Quasi-localised modes (QLMs) in amorphous solids

and landslides.

Figure 4 – Sketch of the process of a shear transformation taken from [31]. When one gradually shears the system (denoted by the thick red arrows), it undergoes elastic deformation first (left) and up to a shear threshold a discontinuous local rearrangement happens (middle) which is irreversible and called a shear transformation. This local rearrangement (right) releases the nonlocal elastic stress, denoted by red arrows, which potentially trigger other transformations.

In the potential energy landscape, a shear transformation process corresponds to tilting the energy barrier until to a saddle-node bifurcation is reached when the curvature becomes flat [32, 33]. A shear transformation occurs when the corresponding particles fall into another minimum. One shear transformation can trigger other shear transformations through releasing of elastic stress field in the far field. It has a four-fold rotation symmetry and its magnitude decays as $\sim 1/r^d$, where $d$ is the spatial dimension, known as the Eshelby kernel [34]. Since this kernel stabilises the solid in some directions and destabilises it in other directions, the density of shear transformations close to a saddle-node bifurcation [35] presents a pseudo gap: [36, 37, 38, 39, 40, 41, 42, 43, 44]:

$$P(x) \sim x^\theta,$$ where $x$ is the additional shear stress needed to trigger a shear transformation. $\theta$ is predicted to depend on the system preparation [40, 45]. From a mean-field elasto-plastic model $\theta = 1/2$ after a quench [48]. $\theta$ also varies continuously as a function of applied external shear in molecular dynamics (MD) simulations [49, 50] as predicted. What remains unknown is how the interaction causing the singular $P(x)$ affects the density of TLS.

0.2 Quasi-localised modes (QLMs) in amorphous solids

The local excitations introduced above correspond to directions in phase space with little restoring forces, suggesting that the low-frequency part of the vibrational spectrum contains information on their respective nature. This view is supported by the early observation that quasi-localised modes (QLMs) [51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62] are present at low-

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**This is a coarse-grained model having a local yield stress in each block [46, 47].**
Introduction

frequencies $\omega$ [63, 64]. Their vibrational amplitudes on particles are essentially localised, and
decay as a power-law in space [54, 65] shown in Fig. 5 (a) and (b). This is why they are called
"quasi-localised".

Density of QLMs

In recent 3D MD simulations, the density of QLMs $D_L(\omega)$ is found to be proportional to $\omega^4$
after a quench [54, 55] at low frequency as displayed in Fig. 5 ††. This $\omega^4$ spectrum is found to
be robust under changes in the preparation temperature [66, 57] and to hold in 2D and 4D [65], and to be not to depend on proximity to the unjamming transition [55, 58, 67].

![Figure 5](image)

Figure 5 – (a) The lowest-frequency QLM in space in black (“only components larger than
a tenth of the mode's maximal component are shown.”). The respective projections of
the mode on the x-y, x-z, and y-z planes are shown using colour. (b) Spatial decay profile of
the lowest-frequency QLM. $|\Psi|$ is the vibrational amplitude on each particle. (c) Density of
vibrational modes $D(\omega) = D_L(\omega) \sim \omega^4$ at low frequency in a small system size. All three plots
are from [54].

The density of QLMs in these 3D glasses at low frequency, after removing the plane waves ‡‡, reads

$$D_L(\omega) \equiv \frac{1}{3N - 3} \sum_{l=1}^{3N-3} \delta(\omega - \omega_l) = A_4 \omega^4, \quad 0 < \omega < \omega_g,$$

where $N$ is the number of particles, $\omega_l$ is the discrete eigen frequency of QLMs, $A_4$ reflects the
number of QLMs, and $\omega_g$ is the upper cutoff of this scaling regime [68].

In the thermodynamic limit ($N$ being an order of Avogadro constant $10^{23}$), QLMs are

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††Specifically, in [54], QLMs are obtained in a small system size which allows eliminating plane waves below a
cutoff frequency $\omega_L \sim N^{-1/3}$, where $N$ is the number of particles in the system, and in [55] QLMs are obtained
by selecting modes below a cutoff participation ratio. The participation ratio indicates the fraction of particles
involved in a mode which is higher for plane waves than for QLMs.

‡‡Note that in amorphous solids Goldstone modes, i.e, plane waves always exist at low frequency whose density
follows Debye theory that $D(\omega) = A_D \omega^2$ where $A_D = 3/\omega_D^3$ and $\omega_D$ is the Debye frequency.
hybridized with plane waves and the latter dominate the low-frequency spectrum \(\text{§§}\). However, QLMs still affect physical properties like scattering [69]. The contribution of QLMs to the specific heat is proportional to \(T^5\) as is presented in [70] at temperature around \(10^{3}K\) \(\text{¶¶}\).

**Theoretical explanations for the density of QLMs**

**Theories for \(\omega^4\) spectrum**

To our knowledge, there are two types of explanations why the density of QLMs in amorphous solids can be proportional to \(\omega^4\). The first one [71, 72] follows the spirit of the "soft-potential model" [73, 74, 75] whose potential energy \(U(s)\) along a QLM direction expanded around its minimum is given by a fourth order polynomial:

\[ U(s) = \frac{1}{4!} \chi s^4 + \frac{1}{3!} \kappa s^3 + \frac{1}{2!} \omega^2 s^2, \tag{3} \]

with parameters \(\chi\), \(\kappa\) and \(\omega\), where \(\omega\) is the frequency of the QLMs. The joint distribution \(P(\omega^2, \kappa, \chi)\) is constrained by the fact that the system is at an energy minimum: \(F(s) = dU/ds = 0\). For a random function \(U\), it is unlikely that the curvature is small at a minimum. Indeed the probability that \(F(s)\) crosses 0 (or any constant) is proportional to \(F'(s) = \omega^2\), leading to \(P(\omega^2, \kappa, \chi) \sim \omega^2\).

After a change of variables from \(\omega^2\) to \(\omega\), one can obtain that the joint distribution \(P(\omega, \kappa, \chi)\) is proportional to \(\omega^3\). If the mode is in a generic meta-stable state, \(\kappa\) and \(\chi\) are not bounded by \(\omega\). After integrating them out, \(D_L(\omega)\) is proportional to \(\omega^3\). If the mode is in the ground state, the cubic coefficient must be bounded: \(|\kappa| < \sqrt{8\chi/3}\omega\) \(\text{†††}\), which indicates that there exists only one minimum. The density of QLMs thus reads

\[ D_L(\omega) = \int \int_{|\kappa| < \sqrt{8\chi/3}\omega} P(\omega, \kappa, \chi) d\kappa d\chi \sim \int \omega^4 \sqrt{\chi} d\chi \sim \omega^4. \tag{4} \]

However, this theory ignores the coupling between QLMs. When the system in a meta-stable state, based on \(P(\omega, \kappa) \sim \omega^3\), we can obtain \(P(x) = \int P(x, \kappa) d\kappa = \int P(\omega, \kappa) \| \frac{d\omega}{d\kappa} \| d\kappa \sim \text{constant} \| \theta \). This \(\theta = 0\) is inconsistent with the singular distribution of \(P(x) \sim x^\theta\), which is established due to the interactions among excitations [36, 37, 38, 39, 40, 41]. Although the \(D_L(\omega) \sim \omega^3\) spectrum was found through MD simulations in poorly prepared glasses [76, 77],

---

\(\text{§§}\)The density of plane waves is proportional to \(\omega^2\) while the density of QLMs is proportional to \(\omega^4\) which decreases faster than the former with lowering \(\omega\). One cannot identify QLMs by looking at the spatial feature shown in Fig. 5 or by comparing participation ratio.

\(\text{¶¶}\)At low temperature and low frequency in glass, anharmonicity highly dominates the quantized excitations.

\(\text{†††}\)\(|\kappa| = \sqrt{8\chi/3}\omega\) is the spinodal condition which satisfies \(dU(s)/ds = 0\) and \(d^2U(s)/d^2s = 0\) at the inflection point.

\(\text{‡‡‡}\)When the system is close to a saddle-bifurcation, \(x \sim \omega^4/\kappa\). \(\chi\) is regarded as a constant since it does not affect \(x\).
Introduction

it was later shown to be a finite size effect, and in large system size the $\omega^4$ spectrum emerges \[78\] §§§.

For a system in its ground state, a simple argument to derive $P(x)$ consistent with their results exists. Since $x \sim \kappa^3 \sim \omega^3$, $P(x) \sim D_L(\omega) \left|\frac{d\omega}{dx}\right| \sim x^{2/3}$ (see the rigorous derivation based on the joint distribution $P(\omega, \kappa) \sim \omega^3$ in A.6.) .

Alternatively, a second approach in obtaining the $\omega^4$ dependence observed in the spectrum of QLMs involves a two step “vibrational instability argument” \[15, 79, 80\] ¶¶¶. (1) First, consider the low-frequency harmonic oscillators with frequency $\omega'$ interacting with their surrounding high frequency modes of characteristic frequency $\omega_D$(through the elastic medium). Due to the interaction and by assuming the density of $\omega'$ smooth, they obtain that the density of the eigen frequency is proportional to $\omega$ when $\omega$ approaches zero. (2) Next, by applying a mean field technique that involves the addition of a quartic term and linearisation of the random mechanical noise contribution in the initial harmonic potential, the authors derive an effective potential that is tilted and possesses a minimum that is shifted from its original position. A further examination of the distribution of frequencies $\omega_{\text{new}}$ evaluated at this new minimum leads to an additional factor in $D_L(\omega_{\text{new}})$, which is proportional to $\omega_{\text{new}}^3$ and thus identical to the contribution of the joint distribution $P(\omega, \kappa, \chi)$ stated above. Finally, by combining these two steps, they obtain $D_L(\omega_{\text{new}}) \sim \omega_{\text{new}}^4$.

Similarly, in the second theory, since the joint distribution at the new minimum is same as $P(\omega, \kappa, \chi)$ in the first theory, it leads to $\theta = 2/3$ that is derived without considering interactions. However, note that the nature of these interactions in this model is still not explicitly considered. Therefore, it is interesting to investigate the power-law behavior of $D_L(\omega)$ and how it varies under shear when these interactions are properly taken into account.

Infinite dimension mean-field theory

The $\omega^4$ scaling in the spectrum is also found in numerics in 3D spin glass \[52\]. However, in infinite dimension, since the spatial fluctuations are negligible, the spectrum of the vibrational modes (instantaneous normal modes) in p-spin glass can be solved exactly \[81\]. It is found that the spectrum becomes gapped for temperatures $T$ below the mode-coupling temperature $T_c$ \[3, 82\]. The gap $\omega_c$ is predicted to grow as $T$ decreases, see Fig. 6, with the relation $\omega_c^2 \sim (T_c - T)$ below $T_c$ \[16, 82, 83\].

This mean-field prediction supports the previous proposal by Goldstein \[84\] that below some temperature $T_c$ near the glass transition most normal modes become stable. Such enhanced stability is consistent with the overall elastic stiffening upon cooling apparent in the shear \[23\] or local \[66\] elastic moduli in fragile supercooled liquids.

§§§In very stable glass, since QLMs are more localised and their distances are large, the interactions between different quasi-localised modes could be neglected. Hence, the finite size effect is insignificant there \[78\].

¶¶¶See the appendix A.3 for detail.
0.3. Effect of preparations on the density of local excitations and QLMs

The density of local excitations is strongly controlled by temperature or system preparation. It is challenging but of practical importance to understand them.

Recently, in [85], the density of TLS $n(E)$ was shown to strongly depend on parent temperature $T_p$ (see Fig. 7 (a)). To make ultrastable glasses, they adopted the state-of-art SWAP Monte Carlo method. The SWAP Monte Carlo method enables two particles to exchange their diameters. It results in the speed-up of the thermal equilibration and allows the production of configurations equilibrated at low $T_p$ in computer simulations [86]. Compared to glasses prepared from high $T_p$, $n(E \to 0)$ is 100 times smaller in ultrastable glasses (at low $T_p$), which would reasonably explain the depletion of TLS in experiments [7, 20] †.

For shear transformations, it was found that density in well-prepared glasses is significantly reduced. This is reflected by the smooth stress-strain curve at small strain and an abrupt stress drop at yielding [87, 88, 89]. In Fig. 7 (b), the stress-strain curves prepared from different $T_p$ are displayed. With the lowering of preparation temperature, glasses become more stable but also more brittle. This results in a sharp transition that appears at yielding which corresponds to a distinct shear band in real space [89].

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At which the system is equilibrated and then quench from this temperature to zero.

The value of $n_0$ in numerical simulation is still $2 - 3$ orders of magnitude larger than its experimental results.
Figure 7 – (a) Density of TLS, (b) stress-strain curves under quasi-statically shearing [35] and (c) $A_4$ at different preparation temperatures. In (b) and (c) glasses are prepared via instantaneous quench from $T_p$ at which equilibrated configurations are obtained through SWAP Monte Carlo protocol. The plots are adapted from [85], [88], and [57], respectively.

With regard to QLMs, besides their $\omega^4$ spectrum in inherent structures of most glasses, it is also found that their prefactor $A_4$ decreases several decades as the parent temperature $T_p$ is reduced by 20% [57, 68]. See Fig. 3 (c) that $A_4$ varies with $T_p$ [57]. Why does $A_4$ decrease so dramatically given only a small reduction in $T_p$? Furthermore, QLMs also display a lower participation ratio upon cooling. A unifying explanation for these facts is currently missing.

The aim of this thesis is to formalise the relation between local excitations and QLMs, and propose tentative answers to the questions shown in italics above.

0.4 Organisation of the thesis

In Chapter 1, we provide a theory for the density of QLMs $D_L(\omega) \sim \omega^\alpha$ at zero temperature, which takes their interactions into account and clarifies their relationship with shear transformations. We predict two distinct regimes, shear transformations are found to be the
dominant source of QLMs only in one of them. We confirm our predictions by independently measuring the exponents $\alpha$ and $\theta$, using molecular dynamics simulations of quasi-statically sheared glasses obtained at distinctly different quench rates.

In Chapter 2, we present a model and protocol that enable the generation of extremely stable computer glasses at minimal computational cost. The protocol consists of an instantaneous quench in an augmented potential energy landscape, with radii as additional degrees of freedom. We find that in our most stable computer glasses, $D_L(\omega)$ is gapped. We explain this observation that is also consistent with the lack of plasticity we observe at small stress.

In Chapter 3, we reconcile the contradiction that the density of QLMs observed in finite dimension is gapless and the one predicted in infinite dimension is gapped. We propose an interpretation of mean-field theories of the glass transition, in which the modes beyond the gap act as an excitation reservoir, from which a pseudo-gap distribution is populated with its magnitude rapidly decreasing at lower $T$. We discuss how this picture unifies the rarefaction as well as the decreasing size of excitations upon cooling, together with a string-like relaxation occurring near the glass transition.

In Chapter 4, preliminary results on the local excitations are presented for glasses obtained by an instantaneous regular quench from an equilibrated configurations at low temperature $T_p$ obtained by the SWAP Monte Carlo method. We find that in these glasses, (i) rearrangements become string-like when the glass becomes more stable. (ii) For small $T_p$, slow annealing does not affect $A_4$. It indicates that the reservoir effect is not the dominant one controlling $A_4$. (iii) One local rearrangement can be associated with several QLMs. (iv) We test the idea that these soft regions are induced by rare fluctuations of key quantities controlling stability, such as coordination and pressure. Our results indicate a clear correlation. Yet, more needs to be done to characterise the geometry of these rare regions. It appears necessary to later estimate how their density depends on the overall stability of the system.

In Chapter 5, I argue that TLS are dominated by nearly symmetric DWPs with a characteristic frequency $\omega_0$. It leads to that the density of TLS, $n_0$, is proportional to $A_4$ and to the fraction $f_{\omega_0}$ of double-wells at $\omega_0$. Based on this relation, I estimate $n_0$ in glasses prepared from different parent temperature $T_p$ obtained by the SWAP Monte Carlo method. I find that $n_0$ decreases by a factor of 300 in ultrastable glasses than poorly prepared glasses with both $A_4$ and $f_{\omega_0}$ playing a significant role. More significantly, the estimations of $n_0$ are consistent with the order of magnitude of the change in $n_0$ found in amorphous silicon.
1 The theory of density of interacting quasi-localised modes in amorphous solids

Abstract

Quasi-localised modes appear in the vibrational spectrum of amorphous solids at low-frequency. Though never formalised, these modes are believed to have a close relationship with other important local excitations, including shear transformations and two-level systems. We provide a theory for their frequency density, \( D_L(\omega) \sim \omega^\alpha \), that establishes this link for systems at zero temperature under quasi-static loading. It predicts two regimes depending on the density of shear transformations \( P(x) \sim x^\theta \) (with \( x \) the additional stress needed to trigger a shear transformation). If \( \theta > 1/4 \), \( \alpha = 4 \) and a finite fraction of quasi-localised modes form shear transformations, whose amplitudes vanish at low frequencies. If \( \theta < 1/4 \), \( \alpha = 3 + 4\theta \) and all quasi-localised modes form shear transformations with a finite amplitude at vanishing frequencies. We confirm our predictions numerically.

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Chapter 1. The theory of density of interacting quasi-localised modes in amorphous solids

1.1 Introduction

Unlike crystals, amorphous solids do not present topological defects due to their lack of long-range order. Instead they display excitations where a group of particles can rearrange. These essentially local excitations lead to a dipolar change of stress in the medium, which can effectively couple them. An example of local excitations is two-level systems that govern the low-temperature properties of glasses, for which the particles’ rearrangement is induced by quantum tunnelling [10, 9, 4]. The nature of two-level systems and the role of their interactions, argued to lead to a pseudo-gap in their density, is still debated [11, 17, 15]. Another example of local excitations is shear transformations [26, 27, 28, 29, 30], in which a rearrangement, or plastic event, can occur in the absence of any quantum or thermal fluctuations by a local increase in stress that triggers a saddle node bifurcation [35]. In this case, the important role of interactions is established: they lead to bursts of avalanches of many plastic events [43, 44]. This behaviour is a necessary consequence [36, 42] of the presence of a pseudo-gap $P(x) \sim x^{\theta}$ in the density of these excitations [37, 38, 39, 40, 41] (where $x$ is the additional shear stress that must be applied locally to trigger a new event). Treating the effect of interactions as a mean-field mechanical noise leads to the prediction that $\theta$ varies non-monotonically as shear stress is applied [48], as confirmed numerically [42, 49, 88].

These local excitations correspond to directions in phase space with little restoring forces, suggesting that the low-frequency part of the vibrational spectrum contains information on their respective nature. This view is supported by the early observation that quasi-localised modes are present at low-frequencies [64], leading to a considerable numerical effort to characterise them. Most studies find that their density follows $D_L(\omega) \sim \omega^\alpha$ with $\alpha = 4$ [51, 52, 53, 54, 55, 56, 57] although $\alpha \approx 3$ has also been reported [76, 77]. Theoretically, it has been argued, for general bosonic disordered systems, that $\alpha = 4$ in the ground state, and $\alpha = 3$ in generic meta-stable states [79, 72]. This theory, however, neglects interactions between quasi-localised modes. Its apparent success thus seems to be at odds with the established role of interactions in determining the properties of plastic deformation and yielding [43, 44, 36, 42, 37, 38, 39, 40, 41].

In this paper, we provide a theory for the density of quasi-localised modes for classical systems at zero temperature, which takes their interactions into account and clarifies their relationship with shear transformations. In particular, we introduce and treat analytically a mesoscopic model of interacting quasi-localised modes. We predict two distinct regimes, shear transformations are found to be the dominant source of quasi-localised modes only in one of them. We confirm our predictions by independently measuring the exponents $\alpha$ and $\theta$, using molecular dynamics simulations of quasi-statically sheared glasses obtained at distinctly different quench rates.
1.2 Mesoscopic model & theoretical prediction

We model an amorphous solid as a collection of mesoscopic blocks whose size is comparable to that of quasi-localised modes. In each block we consider the softest quasi-localised mode. We denote by $s$ the displacement along that mode and by $u_i(s)$ the Taylor expansion of the energy [91] in a block $i$:

$$u_i(s) = \frac{1}{2!} \lambda_i s^2 + \frac{1}{3!} \kappa_i s^3 + \frac{1}{4!} \chi_i s^4 + O(s^5).$$  \hspace{1cm} (1.1)

Numerical measurements of $\chi_i$ have shown that its distribution is narrow [54], we thus assume that it does not depend on $i$, and choose the units of the displacement $s$ so that $\chi = 1$. Consequently $\lambda_i$ and $\kappa_i$ determine the shape the potential. Note that $\lambda_i = m \omega_i^2$ is the smallest eigenvalue of the Hessian of the block where we choose the corresponding mass $m = 1$ as unit.

The shear stress $\sigma_i$ in the block can change either due to a global applied stress or due to an interaction with another block in which a rearrangement occurred. A change of shear stress by $\delta \sigma_i$ tilts the potential $u_i(s)$:

$$\tilde{u}_i(s, \delta \sigma_i) = u_i(s) - s C_i \delta \sigma_i, \hspace{1cm} (1.2)$$

In this scalar approximation, $C_i$ describes the coupling between this mode and the shear stress, and should depend on $i$, and possibly on the value of local stress $\sigma_i$. We neglect these dependencies and impose $C_i = 1$ through a suitable choice of the units of stress. Following ideas presented in [92] we expand the energy around the new minimum. This changes $\lambda_i$ and $\kappa_i$, and in the limit of infinitesimal $\delta \sigma_i$ we obtain the following flow:

$$\frac{\partial \lambda_i}{\partial \sigma_i} = \frac{\kappa_i}{\lambda_i}, \hspace{1cm} \frac{\partial \kappa_i}{\partial \sigma_i} = \frac{1}{\lambda_i}. \hspace{1cm} (1.3)$$

See Appendix B.1 for details. A conserved quantity of this dynamics is:

$$\Phi_i \equiv \kappa_i^2 - 2 \lambda_i. \hspace{1cm} (1.4)$$

Thus, we can track the evolution of the energy shape in each block along the parabolic trajectories in the $(\lambda, \kappa)$ plane. As we illustrate in Fig. 1.1, two distinct behaviours, as previously identified in [92], are separated by the $\Phi = 0$ parabola (black line). $\Phi < 0$ (highlighted in blue) corresponds to ‘passive’ modes that never undergo a saddle node bifurcation. For $\Phi > 0$ (in red) shear transformations occur. In that case a potential with a single minimum (point $A$) evolves under increasing stress to a point where a second minimum appears (point $B$). As the stress increases, the minima become equally deep (point $C$). Eventually, a saddle node bifurcation occurs (point $D$) and the system falls in the other minimum (point $B'$). It is straightforward to show that points $B$ and $B'$ lie on the parabola $\kappa^2 - 8 \lambda / 3 = 0$ (see Appendix B.2), indicated using a dashed green line in Fig. 1.1.

So far we have described how to track the softest quasi-localised mode in each block. However,
Chapter 1. The theory of density of interacting quasi-localised modes in amorphous solids

Figure 1.1 – Illustration of the flow of block parameters in the \((\lambda, \kappa)\) plane, under increasing shear stress. Examples of trajectories are shown on the left. The shape of the associated potentials \(u\) are shown on the right. The blue line is an example of a passive mode, for which \(\Phi < 0\). The red line is an example of a shear transformation, for which \(\Phi > 0\). The black line corresponds to the marginal case for which \(\Phi = 0\). The dashed green line marks the appearance of the second minimum in \(u\), and thus the locations of reinsertion after a failure.

It may happen that the tracked mode becomes stiffer than the next softest mode. This will occur for a typical value of \(\lambda\) that we denote \(\lambda_{\text{min}}\). To implement this effect in the model, if \(\lambda\) reaches \(\lambda_{\text{min}}\) we switch to a new softest mode. We describe its property by choosing its \(\Phi\) randomly from a distribution \(P_0(\Phi)\). We expect that \(P_0(\Phi)\) is a smooth distribution, i.e. that \(P_0(\Phi) > 0\) in the relevant range of \(\Phi\) (without any singularity, in particular around \(\Phi = 0\)).

Following elasto-plastic models [93, 46, 94], we describe the change of shear stress on block \(i\) as \(\delta \sigma_i = d\Sigma + \eta_i\), where \(d\Sigma\) is the increment of globally applied stress, and \(\eta_i\) stems from the rearrangements (saddle node bifurcations) of other blocks. \(\eta_i\) is of zero mean and displays a power-law distribution [37, 48]. During an avalanche of rearrangements \(\delta \sigma_i\) thus performs a random flight. In the mean-field approximation where \(\eta_i\) is assumed to be uncorrelated in space and time, it corresponds to a Lévy Flight, and exact calculations are possible [48]. Our arguments below, however, do not rely on this approximation.

The spectrum of the Hessian, \(P(\lambda)\), can be calculated as a marginal distribution of the density of states \(P(\lambda, \kappa)\). A change of variables allows us to express \(P(\lambda, \kappa)\) in terms of \(\Delta \sigma\) and \(\Phi\):

\[
P(\lambda, \kappa) = 2\lambda P(\Delta \sigma, \Phi), \tag{1.5}
\]

where \(\Delta \sigma\) is the accumulated stress change relative to an arbitrary reference and the factor \(2\lambda\) corresponds to the absolute value of the Jacobian \(|\partial(\Delta \sigma, \Phi)/\partial(\lambda, \kappa)|\) (see Appendix B.3). We first consider passive modes for which \(\Phi < 0\), and for convenience choose to define \(\Delta \sigma\) such that \(\Delta \sigma = 0\) at \(\kappa = 0\). If many rearrangements take place in the system (as expected after a
fast quench or after a succession of avalanches triggered by increasing the stress), then the flights in each block will lead to a finite distribution for \( P(\Delta \sigma) \) at any \( \Phi < 0 \), independently of the initial conditions, as long as \( P_0(\Phi) > 0 \). In particular \( P(\Delta \sigma = 0, \Phi = 0) > 0 \), implying that \( P(\lambda, \kappa) \sim \lambda \) in the limit of vanishing \( \lambda \). Thus the contribution of passive modes to the spectrum of the Hessian is:

\[
P(\lambda) = \int_{\Phi \leq 0} P(\lambda, \kappa) d\kappa \sim \lambda \int_{\kappa \leq \sqrt{\lambda}} d\kappa \sim \lambda^{3/2}.
\] (1.6)

For a fixed \( \Phi > 0 \), failure occurs when \( \lambda = 0 \). An example is shown in Fig. 1.1 as point \( D \) and its mirror image \( D' \). Thus the dynamics after a fast quench or a big avalanche corresponds to a stochastic walk with absorbing conditions at these points, and reinsertion in points \( B' (B) \) if failure happened in \( D (D') \).

We then identify \( x = \Delta \sigma - \Delta \sigma|_{\lambda=0} \) as the additional stress needed to trigger a shear transformation. The density of states can be shown to display a power-law between the absorption and reinsertion points \( D \) and \( B^\dagger \). From [48] we know that \( P(x, \Phi) \sim (x/x^*)^\theta \) for \( x < x^* \), where \( x^* \) corresponds to point \( B \). For \( x \gg x^* \), \( P(x) \) will vary smoothly. It is straightforward to show that \( x^* \sim \Phi^{3/2} \) and that for \( x \ll x^*, x \sim \lambda^2/\kappa \) and \( \Phi \sim \kappa^2 \) (see Appendix B.4). Using Eq. (1.5) we finally obtain:

\[
P(\lambda, \kappa) \sim \frac{\lambda^{2\theta+1}}{\kappa^{4\theta}} \text{ for } \lambda \ll \kappa^2.
\] (1.7)

Eq. (1.7) readily gives the contribution of shear transformations to the spectrum of the Hessian:

\[
P(\lambda) = \int_{\Phi > 0} P(\lambda, \kappa) d\kappa \sim \begin{cases} 
\lambda^{2\theta+1} & \text{for } \theta < 1/4 \\
\lambda^{3/2} & \text{for } \theta \geq 1/4.
\end{cases}
\] (1.8)

Thus if \( \theta < 1/4 \), shear transformations dominate the low-frequency spectrum of the Hessian. Following Eq. (1.7), the integral in Eq. (1.8) is dominated by large \( \kappa \), implying that shear transformations leading to large plastic events are observed as \( \lambda \to 0 \). By contrast, for \( \theta \geq 1/4 \) both shear transformations and passive modes contribute equally. In that case the integral in Eq. (1.8) is dominated by small \( \kappa \sim \sqrt{\lambda} \), implying that low-frequency shear transformations lead to tiny rearrangements. Concerning the density of vibrational modes, using \( \omega^2 \sim \lambda \) and Eqs. (1.6,1.8) we get:

\[
D_L(\omega) = P(\lambda) \frac{d\lambda}{d\omega} \sim \omega^\alpha, \quad \alpha = \begin{cases} 
4\theta+3 & \text{for } \theta < 1/4 \\
4 & \text{for } \theta \geq 1/4.
\end{cases}
\] (1.9)

Note that in the absence of interactions \( \theta = 0 \), and consequently our result is consistent

---

1 Blocks are also inserted at \( \lambda = \lambda_{\text{min}} \) as discussed earlier. However, as long as a finite fraction of blocks are reinserted they give a dominant contribution to the density of states. For example, in a mean-field approximation blocks perform Lévy Flight of index \( \mu = 1 \) [48] in which diffusion and drift are comparable so that a finite fraction of blocks fails in opposite direction of the drift and is reinserted.
with the theoretical prediction for non-interacting modes $\alpha = 3$ [79, 72]. In the presence of interactions $\theta$ will generally be nonzero and will depend on the system preparation. The latter allows us to test our theory, which we now do using molecular dynamics simulations for different preparation protocols.

### 1.3 Molecular dynamics

As mentioned in the introduction, mean-field theory predicts that $\theta = 1/2$ after a quench, then drops and rises again as a function of the applied shear strain $\gamma$ [48]. The drop is expected to be more pronounced for well-annealed glasses [48], as confirmed numerically [42, 49, 88]. To test our theory we thus measure $\alpha$ and $\theta$ as a function of $\gamma$ for glasses obtained using different preparations. We consider the three-dimensional bi-disperse glass of [76], composed of $N$ particles interacting by purely repulsive inverse power-law potentials, which are continuous up to the third derivatives. We consider two distinct preparation protocols: (i) a rapid quench, that results in a poorly annealed glass, obtained by a steepest descent after instantaneously cooling from a temperature $T = T_0$ (higher than the glass transition temperature) to $T = 0$; and (ii) a slow quench, that results in a better annealed glass, obtained by first cooling it at a low rate from $T = T_0$ to $T = T_0/10$, followed by a steepest descent to remove the remaining heat. Details are provided in the Appendix B.5.

After the glass is prepared, we quasi-statically apply a simple shear using Lees-Edwards periodic boundary conditions [95]. As commonly reported, we find that the stress-strain curve $\langle \Sigma(\gamma) \rangle$ is monotonic after a rapid quench and displays an overshoot after a slower quench, as shown in Figs. 1.2(a,b). The pseudo-gap exponent $\theta$ is readily extracted using extreme value statistics [38, 40], which uses the fact that $\langle x_{\text{min}} \rangle \sim N^{1/(1+\theta)}$, where $x_{\text{min}}$ characterises the shear transformation closest to an instability. More precisely, it is the additional stress needed to trigger the next plastic event. It is proportional to the strain increment between events, $\gamma_{\text{min}}$, illustrated in the inset of Fig. 1.2(a). $\langle \gamma_{\text{min}}(N) \rangle$ is reported in Figs. 1.2(c,d), from which the exponent $\theta$ is extracted via a power-law fit. The result is reported in Fig. 1.3(a,b) where the predicted non-monotonicity of $\theta(\gamma)$ is observed. We find that for the rapidly quenched glass, $\theta > 1/4$ for all $\gamma$, leading to the prediction that $\alpha = 4$. By contrast, the slowly quenched glass displays a range of strains for which $\theta < 1/4$, where our prediction is that $\alpha < 4$.

To measure the exponent $\alpha$, we diagonalise the Hessian to obtain $D_L(\omega)$. We then determine $\alpha$ in two ways. One way is to use the fact that the mean lowest frequency scales with the system size as $\langle \omega_{\text{min}} \rangle \sim N^{-(1+\alpha)}$. We show this scaling at three representative values of strain $\gamma$ in Figs. 1.2(e,f) and measured values of $\alpha$ are shown as blue line in Figs. 1.3(c,d).

The exponent $\alpha$ can also be measured directly from $D_L(\omega)$, in contrast to $\theta$, that cannot be obtained directly from the distribution $P(\gamma_{\text{min}})$, as we explain in Appendix B.6. However, this measurement is challenging as it is polluted by the influence of plane waves and by finite size effects at low frequencies (see Figs. 1.2(g,h) and Appendix B.7). In order to perform this measurement, we follow a protocol [55] that separates quasi-localised modes from plane waves.
1.3. Molecular dynamics

Figure 1.2 – (a,b) Stress-strain curves averaged over 1000 realisations for different \( N \) (see legend). (c,d) Finite size scaling of the mean strain increment between plastic events \( \langle \gamma_{\text{min}} \rangle \) at three representative applied strains to determine \( \theta \) (see legend). (e,f) Finite size scaling of the mean lowest frequency is used at three representative strains \( \gamma \) to determine \( \alpha \) (see legend). (g,h) Density of quasi-localised modes \( D_L(\omega) \) at low frequencies \( \omega \): (g) 1000 realisations at \( N = 16000 \) and (h) 5000 realisations at \( N = 32000 \). Modes with a participation ratio above the threshold (g) \( e_c = 0.125 \) and (h) \( e_c = 0.0625 \) have been removed following the procedure of [55]. Insets of (g,h) show participation ratios \( e \) and their thresholds \( e_c \) (solid black lines). The green markers on the axes of (g,h) indicate the fitting range of \( \omega \).
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based on their participation ratio $e \equiv 1/(N \sum_j (\Psi_j^2)^2)$, where $\Psi_j$ is the eigenmode component on the $j$th particle. Examples of participation ratios are shown in insets of Figs. 1.2(g,h) where the employed threshold $e_c$ is indicated by a horizontal line. We have verified robustness of our results below by raising and lowering $e_c$ by 20%. $\alpha$ is fit on the ‘filtered’ $D_L(\omega)$, whereby the fitting range is bounded on the upper side by the point where the power law scaling is clearly interrupted by the plane waves. A range of lower bounds has been used for which the measurement of $\alpha$ is robust (see Appendix B.8 for details). The employed fitting range is indicated using green bars in Figs. 1.2(g,h).

The results, in Fig. 1.3(c,d), show that the two different measurements of $\alpha$ are in a good qualitative agreement. The results are consistent with our theoretical prediction for $\alpha$. In rapidly quenched systems $\alpha = 4$, also true in the steady state (shown in Appendix B.9), while in slowly quenched systems we find that $\alpha$ is significantly smaller than 4 precisely in the range where $\theta < 1/4$. To our knowledge, this is the first time that such a non-monotonic behaviour of $\alpha$ as a function of shear has been measured directly from MD simulations.

Figure 1.3 – (a,b): Exponent $\theta$ extracted by finite size scaling of $\langle \gamma_{\text{min}} \rangle$ at different $\gamma$. The employed system sizes are reported in the legends. (c,d): Green line: $\alpha$ based on measured $\theta$. Blue line: $\alpha$ extracted by finite size scaling (FSS) of $\langle \omega_{\text{min}} \rangle$ at different $\gamma$ using system size range $N = 2000, 4000, 8000, 16000$ and $N = 4000, 8000, 16000, 32000$. Red line: $\alpha$ obtained from a direct fit $D_L(\omega)$ at $N = 16000$ and $N = 32000$. Our prediction for $\alpha$ is indicated using a solid green line. The error bars for $\theta$ and $\alpha$ correspond to 95% confidence intervals for the coefficient estimates obtained by linear fit on a log-log scale.
1.4 Conclusion

We have provided a theory for the density of localised soft modes in classical amorphous solids at zero temperature.

Our approach goes beyond previous ones by taking long-range interactions between these modes into account. We have found two regimes, one in which modes near a saddle-node bifurcation are dominant, and one in which they contribute to a finite fraction of the spectrum (the rest consisting of passive modes that are irrelevant as far as plasticity and two-level systems are concerned). The first regime does not appear in rapidly quenched materials (and is thus presumably absent in foams and granular materials). By contrast it is expected to be very pronounced in real glasses which are much more stable than the ‘slowly quenched’ configurations studied here. This view is supported by recent measurements in simulated glasses prepared by a swap algorithm (that are comparable to experimental cooling rates), which indeed show extremely small values for $\theta$ [88]. Note that our argument appears to be rather generic, and may apply to other disordered systems with long-range interactions, e.g. in crystals with defects.

Our work is a necessary first step to describe systems at finite temperatures or shear rates. For example, it is interesting to reflect on the role of thermal fluctuations in a perturbative manner, if a very small temperature would have been switched on in the configurations we have described. Modes in which the high energy well is occupied would eventually switch states (an effect that is faster for small $\lambda$ and $\kappa$ where barriers are small and activation is fast). In the $(\lambda, \kappa)$ plane this would lead to a depleted region, whose right border corresponds to a limiting parabola where wells are of equal depth (including point C and the origin Fig. 1.1). In time the depleted region will grow away from the origin and a pseudo-gap may open at the limiting parabola [96, 17, 65]. Away from this region we expect our described solutions to hold. Measuring the joint distribution $P(\lambda, \kappa)$ for this kind of protocol, a task for which recent numerical methods are being designed [76], would shed light on the nature of bottom of the energy landscape in glasses.
2 Fast generation of ultrastable computer glasses

abstract

We present a model and protocol that enable the generation of extremely stable computer glasses at minimal computational cost. The protocol consists of an instantaneous quench in an augmented potential energy landscape, with particle radii as additional degrees of freedom. We demonstrate how our glasses’ mechanical stability, which is readily tunable in our approach, is reflected both in microscopic and macroscopic observables. Our observations indicate that the stability of our computer glasses is at least comparable to that of computer glasses generated by the celebrated Swap Monte Carlo algorithm. Strikingly, some key properties support even qualitatively enhanced stability in our scheme: the density of quasilocalized excitations displays a gap in our most stable computer glasses, whose magnitude scales with the polydispersity of the particles. We explain this observation, which is consistent with the lack of plasticity we observe at small stress. It also suggests that these glasses are depleted from two-level systems, similarly to experimental vapor-deposited ultrastable glasses.

*This chapter is taken from our published article [97] (DOI: 10.1103/PhysRevE.99.012106).
I got involved in discussion with Edan Lerner and Matthieu Wyart in general in this article and in particular on the gapped density of vibrational modes section of this article.
List of authors: Geert Kapteijns, Wencheng Ji, Carolina Brito, Matthieu Wyart, and Edan Lerner.
Chapter 2. Fast generation of ultrastable computer glasses

2.1 Introduction

One of the key challenges in glass physics is understanding the large variations of the thermodynamic, micro- and macro-mechanical properties that glassy solids often display, depending on the protocol by which they are formed. Pronounced examples of this dependence are seen in metallic glasses: their toughness can depend in a complex manner on the degree of annealing of the pre-deformed samples [98, 5], a phenomenon attributed to ‘annealing embrittlement’ [5]. In numerical simulations of nanoindentation of a model metallic glass it was observed that the propensity for strain localization in the form of shear banding is substantially enhanced by deeper annealing of the pre-deformed glassy samples [99]. In computer glasses made by quenching equilibrium supercooled configurations of various temperatures, it was observed that the frequencies of soft quasi-localised modes increase significantly for more deeply supercooled parent equilibrium states [66], while the spatial extent of those modes decreases [100]. The low-temperature thermodynamics of vapor-deposited ultrastable glasses provide another striking example of the effects of preparation protocol: the temperature dependence of their specific heat resembles that of crystalline solids [7, 101] instead of the ubiquitous anomalous dependence that is generically observed in glassy solids [8, 10].

A recent groundbreaking advancement in computer simulations of supercooled liquids has made it possible to equilibrate supercooled liquids down to extremely low temperatures, surpassing even experimentally accessible supercooling temperature ranges [86]. This breakthrough has been achieved by employing the Swap Monte Carlo algorithm [102, 103, 104], and — building on previous observations made in [105] for a three-component mixture — carefully tailoring a model glass former such that the efficiency of the algorithm is maximized, while ensuring that the model remains robust against crystallization or fractionation. Computer glasses formed via this computational approach display very large variations in their transient elasto-plastic response. In particular, a phase transition manifested by the nucleation of a system-spanning shear band in deformed samples is observed, depending on the temperature from which the initial, undeformed glassy samples were quenched [88]. Furthermore, a study of the vibrational spectra of Swap Monte Carlo computer glasses revealed that the density of quasi-localised vibrational modes, previously shown to follow a universal non-Debye distribution \( D(\omega) \sim \omega^{-5}\omega^4 \) [54, 65], is reduced with deep supercooling — it retains the same power-law behavior, but the coefficient \( \omega^{-5} \) diminishes severalfold [57].

While the Swap Monte Carlo approach allows one to generate computer glasses with unprecedented stability, the accessible system sizes are inevitably limited by slow glassy dynamics at very deep supercooling. In this work we describe a computational approach, proposed by some of us in [106], that consists of a direct minimization of an augmented potential energy in which the particle radii are included as additional degrees of freedom. This approach enables the generation of computer glasses that are as stable as those created via Swap Monte Carlo, at a small fraction of the computational cost. We study the structure, micro- and macro-mechanical properties of our computer glasses, demonstrating the large variation in glass stability that our approach provides. On the practical side, the computational speed-up offered
by our approach will enable extensive statistical analyses of large ensembles of glassy samples. Using our approach very large and stable glassy samples can be generated, which will likely be useful for computational studies of transient dynamics and shear-banding instabilities under external deformations. On the physical side, our key finding is that the ultra-stable glasses we generate have a gap in their density of quasi-localised excitations: the behavior \( D(\omega) \sim \omega^{-5/2} \) breaks down below some frequency scale \( \omega_\Delta \). We show that \( \omega_\Delta \sim \Delta^{1/2} \), where \( \Delta \) characterizes the amount of polydispersity. This result rationalizes why there is so little pre-yielding plasticity in these glasses, and suggests that they are also deprived of two-level systems, in consistence with recent empirical observations in vapor-deposited ultrastable glasses [7, 101].

This paper is organized as follows; we first provide a detailed description of the computer model employed and the protocol by which we created glassy samples in Sect. 2.2. In Sect. 2.3, we present various micro- and macro-structural analyses of our computer glasses, including an analysis of the vibrational spectra. We present results from athermal quasistatic shear deformation of our computer glasses in Sect. 2.4. We rationalize the scaling of the frequency gap featured by quasi-localised excitations in Sect.2.5.

### 2.2 Model description and numerical procedures

In this Section we describe the computer glass model employed, and the procedure used to generate ultra-stable glassy samples. Details about the observables measured and presented in our work can be found in Appendix C.1, while in Appendix C.2 we explain the athermal, quasistatic deformation protocol that we used.

#### 2.2.1 Model

A polydisperse liquid of particles in three dimensions is usually thought as having three degrees of freedom per particle, and the particle radii or effective sizes are considered to be frozen parameters. However, in an equivalent description all particles are identical (or, in our work, come in two species to suppress nucleation) but their radii are degrees of freedom subjected to a chemical potential, chosen so as to reproduce the desired polydispersity [107, 108, 106]. Inspired by this description, we consider a system of \( N \) particles in three dimensions (3D) that interact via the potential energy

\[
U = \sum_{i<j} \varphi(r_{ij}, \lambda_i, \lambda_j) + \sum_i \mu(\lambda_i, \lambda_{i}^{(0)}),
\]

where \( r_{ij} \) is the distance between the \( i^{th} \) and \( j^{th} \) particles, and \( \lambda_i \) is the \( i^{th} \) particle's effective size. During the preparation of our glasses, the particles' effective sizes are considered to be degrees of freedom, as explained in what follows. For the pairwise interactions we use a
Chapter 2. Fast generation of ultrastable computer glasses

modified Lennard-Jones (LJ) potential, which reads

\[
\varphi(\mathbf{r}_{ij}, \lambda_i, \lambda_j) = \begin{cases} 
6 \varepsilon \left( \frac{\lambda_{ij}}{\mathbf{r}_{ij}} \right)^{12} - \left( \frac{\lambda_{ij}}{\mathbf{r}_{ij}} \right)^{6} + \sum_{\ell=0}^{3} c_{2\ell} \left( \frac{\lambda_{ij}}{\mathbf{r}_{ij}} \right)^{2\ell}, & \mathbf{r}_{ij} < x_c \\
0, & \mathbf{r}_{ij} \geq x_c
\end{cases}
\] (2.2)

where \(\varepsilon\) is a microscopic energy scale, \(\lambda_{ij} \equiv \lambda_i + \lambda_j\), and the coefficients \(c_{2\ell}\) are determined by requiring that three derivatives of \(\varphi\) with respect to the interparticle distance vanish continuously at the dimensionless cutoff \(x_c\). For the sake of computational efficiency we chose \(x_c = 2.0\), instead of the traditional \(x_{LJ} = 2.5\) [109].

\[\text{Figure 2.1 – (a) Pairs of nearby particles in our model glass former interact via the pairwise potential } \varphi(\mathbf{r}_{ij}, \lambda_i, \lambda_j) \text{ as given by Eq. (2.2), represented here by the thick blue line. We also plot the canonical Lennard-Jones potential (thin line) for comparison. (b) During the preparation of our glassy samples we allow the effective size degrees of freedom } \lambda_i \text{ to change; their fluctuations are governed by the potential } \mu(\lambda_i, \lambda_i^{(0)}) \text{ given by Eq. (2.3), and plotted here for various values of the stiffness } k_\lambda \text{ as indicated by the legend.}\]

The effective sizes \(\lambda_i\) are subjected to the potential

\[
\mu(\lambda_i, \lambda_i^{(0)}) = \frac{1}{2} k_\lambda (\lambda_i - \lambda_i^{(0)})^2 \left( \frac{\lambda_i^{(0)}}{\lambda_i} \right)^2,
\] (2.3)

where \(\lambda_i^{(0)}\) is the energetically-favorable effective size of the \(i\)th particle in the absence of other interactions, and \(k_\lambda\) is the stiffness associated with the effective size degrees of freedom (DOF). We will demonstrate in what follows that \(k_\lambda\) plays a crucial role in determining the stability of our computer glasses. The potentials \(\varphi(\mathbf{r}_{ij}, \lambda_i, \lambda_j)\) and \(\mu(\lambda_i, \lambda_i^{(0)})\) are plotted in Fig. 2.1. We emphasize that in order to maintain a fixed equilibrium polydispersity, the potential \(\mu\) should in general depend on temperature and pressure. (However, we expect the variations of \(\mu\) to be small in the realistic setting of fixed pressure and varying temperature. In that case, fixing \(\mu\) corresponds to a system of particles that slightly dilate with temperature, an effect which is unlikely to significantly affect properties near the glass transition.) By quenching at fixed \(\mu\) from some temperature \(T\) as we do, we generate inherent structures characterizing the landscape at that temperature, structures that turn out to be ultra-stable.
2.3. Structural analyses and elasticity

We employ a 50:50 mixture, such that one half of the particles have $\lambda^{(0)} = 0.5$, and the other half have $\lambda^{(0)} = 0.7$, expressed in microscopic units of length $\ell$. All particles share the same mass $m$, and times are expressed in terms of $\sqrt{m\ell^2/\varepsilon}$. All physical observables presented in what follows should be understood as expressed in terms of the relevant microscopic units.

2.2.2 Glass preparation protocol

We created glassy samples as follows: we begin by fixing the number density $\rho = N/V$ (with $V$ the system's volume) at 0.5, and performing a high-temperature ($T = 1.0$) equilibration of the system subjected to the potential energy $U$. For this part of the preparation protocol we choose the mass associated with the size DOF to be unity for all particles. We then employ the FIRE algorithm [110] to minimize the potential energy $U$. This minimization is done while fixing the imposed pressure at $p = 1.0$ using a Berendsen barostat [111], with a time constant $\tau_{\text{Ber}} = 10.0$. States are deemed to be in mechanical equilibrium when the ratio of the typical gradient of the potential to the typical interparticle force drops below $10^{-12}$. Crucially, upon convergence of the minimization of the potential energy $U$, we freeze the effective size DOF for all subsequent analyses and simulations, reducing the potential energy to

$$U = \sum_{i<j} \varphi(r_{ij}, \lambda_i, \lambda_j), \quad (2.4)$$

where the pairwise potential $\varphi$ given by Eq. (2.2) remains unchanged. Notice that, in contrast with $U$, $U$ does not depend on the target effective sizes $\{\lambda^{(0)}_i\}$. By construction, configurations found by minimizing the potential $U$ with respect to particle coordinates and effective sizes also correspond to local minima of the reduced potential $U$.

We carried out the procedure explained above while systematically varying the stiffness $k_\lambda$ between 10 and $10^5$. We have also created glasses in which the size DOF are completely frozen during glass formation, corresponding to the limit $k_\lambda \rightarrow \infty$. For the structural analyses and elasticity calculations discussed in the next section, we generated 42,000 independent glassy samples of $N = 4000$ particles for each value of the stiffness $k_\lambda$. For the shear-deformation experiments presented in Sect. 2.4, we generated a few tens of larger systems of $N = 256000$ particles for values of $k_\lambda$ between 10 and $10^4$, in addition to a hundred solids of $N = 16000$ particles for values of $k_\lambda$ between $10^2$ and $10^5$.

2.3 Structural analyses and elasticity

2.3.1 Structure

Our choice of chemical potential $\mu$ (parametrized by the stiffness $k_\lambda$, see Eq. (2.3)) fixes the distribution of radii of the obtained inherent states, as we now characterize. Fig. 2.2 shows the distributions $p(\lambda)$ of effective particle sizes $\lambda$. As the stiffness $k_\lambda$ associated with the effective size DOF is reduced, the width of the distributions grows. In the large-$k_\lambda$ limit, we find $\Delta \sim k_\lambda^{-1}$, where $\Delta$ is the polydispersity (see figure caption for details), consistent with the prediction.
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put forward in [106]. We find that below $k_{\lambda} \approx 10^2$, the two peaks corresponding to 'large' and 'small' particles start to overlap.

Figure 2.2 – Distributions $p(\lambda)$ of particles’ effective size degrees of freedom, plotted against the dimensionless effective size $\lambda \rho^{1/3}$, for various values of $k_{\lambda}$ as indicated by the arrows. The dashed lines represent the distributions measured for particles whose target effective size during glass preparation was $\lambda^{(0)} = 0.5$, and the solid lines represent those for which $\lambda^{(0)} = 0.7$. Inset: the polydispersity $\Delta$ is defined as the ratio of the effective sizes’ standard deviation to their mean. We report $\Delta$ for 'small' and 'large' particles, and the total polydispersity (calculated as the standard deviation to mean ratio, taken over all particles), vs. the stiffnesses $k_{\lambda}$.

Figure 2.3 – Pair correlations $g(r)$ between pairs of 'large' particles (i.e. those with a target effective size $\lambda^{(0)} = 0.70$ during glass preparation) measured in our glassy samples, plotted against the rescaled pairwise distances $r \rho^{1/3}$ for various values of the stiffness $k_{\lambda}$, increasing from thin to thick lines. We find no ordering upon decreasing $k_{\lambda}$. The inset shows how the density $\rho = N/V$ of our glassy samples increases as $k_{\lambda}$ is reduced. The horizontal dashed line marks the density of our $k_{\lambda} = \infty$ glasses.
Next we study the pair correlation function $g(r)$ for various values of $k_\lambda$ in Fig. 2.3. As traditionally done, we calculated the pair correlations for pairs with the same ‘large’ effective target size, the same ‘small’ effective target size, and for different (‘large’-'small’) effective target sizes. In the figure we only present the ‘large’-'large’ correlation function; the other two have similar features. We find that varying $k_\lambda$ does not seem to introduce any observable ordering. In fact, for smaller $k_\lambda$ the second and third peaks of $g(r)$ are diminished. We conclude that all of our constructed glassy samples are disordered.

### 2.3.2 Macroscopic elasticity

We next turn to examining the elastic properties of our glassy samples. We focus first on characterizing the degree of structural frustration that our glasses possess, as manifested by their sample-to-sample shear stress fluctuations. In particular, we are interested in assessing whether allowing for size fluctuations of the particles during glass formation reduces in some way the degree of structural frustration. In order to meaningfully compare between different system sizes and the ensembles created with different values of the size DOF stiffness $k_\lambda$, we calculate a system-size-independent and dimensionless sample-to-sample standard deviation of the shear stress by rescaling the dimensionful standard deviation $\delta\sigma$ by $1/\sqrt{N}$ and the athermal shear modulus $G$:

$$\tilde{\delta}\sigma \equiv \sqrt{N} \delta\sigma / G. \quad (2.5)$$

For the definition of $G$ and other elastic moduli, see Appendix C.1. In Fig. 2.4a we plot $\tilde{\delta}\sigma$ vs. the stiffness $k_\lambda$. As expected, lowering $k_\lambda$ results in more optimally packed glasses with a lower degree of structural frustration, as expressed by a decrease of a factor of two of the shear stress fluctuations over the entire range of $k_\lambda$.

We next study the athermal elastic moduli of our glassy samples. In Fig. 2.4b we report a dimensionless and system-size-independent characterizer of shear modulus fluctuations, defined as

$$\tilde{\delta}G \equiv \sqrt{N} \delta G / G. \quad (2.6)$$

Remarkably, the relative fluctuations decrease by over a factor of 4 across the entire sampled range of $k_\lambda$, suggesting that the increased stability of our glasses with decreasing $k_\lambda$ is accompanied by a strong reduction of coarse-grained local elastic moduli fields.

In Fig. 2.4c we plot the sample-to-sample mean of our glasses’ athermal shear to bulk moduli ratio (see definitions in Appendix C.1). The ratio appears to increase above the $k_\lambda = \infty$ value — represented by the horizontal dashed line — by approximately 85%, which amounts to a variation of the glasses’ Poisson’s ratio from $\nu \approx 0.4$ for $k_\lambda = \infty$ to $\nu \approx 0.32$ for $k_\lambda = 10$, as reported in Fig. 2.4d. We emphasize that all of the above elastic properties show significant change over the range of measured $k_\lambda$, but start to saturate at around $k_\lambda = 10^2$. We will see that this behaviour is consistent with our other measurements in the sections below.
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2.3.3 Vibrational spectra

The stability of disordered solids is often characterized in terms of the statistical properties of low-frequency vibrational modes that emerge due to the solids’ disordered microstructure [112, 113, 66, 57]. In particular, the destabilizing effect of internal stresses and structural frustration has been captured by Effective Medium [113] and mean-field [114] calculations, that predict a gapless spectrum $D(\omega) \sim \omega^2$ of non-phononic (i.e. disorder-induced) vibrational modes. However, numerical results in spatial dimensions $\bar{d} \leq 4$ indicate that the non-Debye low-frequency spectrum (obtained by eliminating Goldstone modes, by considering small systems [54, 65] or by selecting modes based on their participation ratio [55, 57]) of generic structural computer glasses follows a universal $D(\omega) \sim \omega^4$ form, independent of model [54], preparation protocol [66, 57], proximity to the unjamming transition [55], and spatial dimension [65]. The modes that populate the $\omega^4$ tails have been shown to be quasi-localised [54, 65], have been argued to control elasto-plastic responses of externally loaded-glasses [115, 90] and the singularities observed in nonlinear elastic moduli [116]. Furthermore, they are believed [92, 70, 117, 52] to serve as the tunneling two-level systems responsible for the universal anomalous thermodynamics of glasses below a few Kelvin [8, 10].

Figure 2.4 – Elastic properties of our glassy samples: (a) sample-to-sample standard deviation of the dimensionless shear stress $\tilde{\sigma}$ (see text for definition and discussion), vs. the stiffness of the size DOF $k_\lambda$. (b) $\tilde{\sigma}$ is the sample-to-sample standard deviation to mean ratio of the shear modulus, scaled by $\sqrt{\bar{N}}$. (c) Sample-to-sample mean of the ratio of shear to bulk moduli. (d) Sample-to-sample mean Poisson's ratio of our glassy samples. The horizontal dashed lines represent the $k_\lambda = \infty$ values in all panels.
We study the statistics of non-phononic low-frequency vibrational modes of our glassy samples. We have calculated the Hessian matrix $\mathcal{M} = \partial^2 U / \partial \mathbf{x} \partial \mathbf{x}$ of each member of our ensembles of 42,000 glassy solids, and calculated the first 120 vibrational modes (excluding the three translational zero modes). The resulting spectra are plotted in Fig. 2.5a. We find that as $k_\lambda$ is decreased, a gap forms at low frequencies. This indicates that for our small-$k_\lambda$ glassy samples, quasi-localised modes are strongly depleted.

In Fig. 2.5b we show that the gap $\omega_\Delta / k_\lambda \sim 1 / \sqrt{k_\lambda}$ opens in $D(\omega)$ as the collapse indicates. Here we plot $D(\omega)$ for $k_\lambda = 10^5, 3 \times 10^4$ and $10^4$. For smaller $k_\lambda$, the occurrence of the lowest-frequency phonons in $D(\omega)$ destroys the collapse. Inset: numerical validation of the frequency independence of the particle-wise mean squared variation of the forces $f_i = -\partial U / \partial \lambda_i$, induced by a quasi-localised vibrational mode of frequency $\omega$ in $k_\lambda = \infty$ glasses, see discussion in Sect. 2.5.
2.3.4 Nonaffine displacements

Our measurement of the vibrational density of states in Sect. 2.3.3 was limited to the range $k\lambda \geq 10^3$ since the lowest-frequency phonons hinder a clear observation of the further depletion of quasi-localised modes upon decreasing $k\lambda$ beyond $k\lambda = 10^3$. We therefore supplement the measurements of the vibrational density of states with a study of the statistics of particles’ linear displacement responses to forces that emerge following an imposed shear deformation, often referred to as the nonaffine displacements, and denoted here by $v$. Nonaffine displacements are defined as

$$v = -\mathcal{M}^{-1} \cdot \frac{\partial^2 U}{\partial x \partial \gamma},$$

where $\gamma$ parametrizes the imposed shear deformation, see details in Appendix C.2. The main contributions to the contraction of $\mathcal{M}^{-1}$ with $\partial^2 U/\partial x \partial \gamma$ are expected to stem from soft quasi-localised modes, rather than from low-frequency phonons [116]. The statistics of nonaffine displacements are therefore expected to echo those of soft quasi-localised vibrational modes.

In Fig. 2.6 we show the particle-wise distributions of nonaffine displacements squared $v^2\equiv v_i \cdot v_i$ (no summation on $i$ implied). We indeed find that the form of the large-value tails of these distributions mirror the observed gaps in the density of vibrational modes as shown in Fig. 2.5. Here, however, we are able to meaningfully probe the full range of $k\lambda$ compared to the limited range shown in Fig. 2.5. We further see the beginning of the saturation of the stabilizing effect below $k\lambda = 10^2$, consistent with the behavior of the elastic properties reported in Fig. 2.4.

There is an intimate relation between nonaffine displacements and the shear modulus: $G \propto \partial^2 U/\partial \gamma^2 + v \cdot \partial^2 U/\partial x \partial \gamma$ [118]. The substantial reduction in the extreme values of the nonaffine displacements observed upon reducing $k\lambda$ correlate with the decrease in sample-to-sample fluctuations of the shear modulus as seen in Fig. 2.4b. We observe a saturation in both quantities for $k\lambda \leq 10^2$. 

![Figure 2.6 – Particle-wise distributions $p(v^2)$ of nonaffine displacements squared $v^2$, plotted against the dimensionless displacements squared $v^2 \rho^{2/3}$, measured in our ensembles of glassy samples with various values of the size DOF $k\lambda$, increasing from thin to thick lines.](image-url)
2.4 Elasto-plastic transients

In this Section we put the mechanical stability of our ultrastable glasses to a direct test. We employ systems of 256,000 particles and deform them under simple shear strain using an athermal quasistatic protocol as described in Appendix C.2. The results are presented in Fig. 2.7 for glasses made with $k_\lambda = 10^4, 3 \times 10^3, 10^3$ and $10^1$ in panels (a)-(d), respectively. Stress-strain curves for $k_\lambda = 10^2$ are displayed in Fig. C.1 of Appendix C.2. In these plots we rescaled the stress by its average steady-state value.

Glasses created with $k_\lambda = 10^4$ show a monotonic increase of the stress as deformation proceeds. For $k_\lambda = 3 \times 10^3$ there is a mild stress overshoot, and for $k_\lambda \leq 10^3$, we observe a stress overshoot terminated by the occurrence of a macroscopic stress drop signaling the nucleation of a system spanning shear band at a characteristic strain that increases with decreasing $k_\lambda$. We note that Fig. 2.7 only presents data from samples whose shear band is parallel to the $x$-$z$ plane; when the shear band is parallel to the $x$-$y$ plane, the stress does not attain a plateau value after the shear band nucleation, which is an artefact of the geometry of the Lees-Edwards periodic boundary conditions employed \(^\dagger\), as shown in Appendix C.2.

The stability of our glasses can be quantified by the relative magnitude of the stress drop, i.e. the

\(^\dagger\)We thank Misaki Ozawa for pointing out this detail.
ratio between the height of the stress peak and the following steady-state stress. This ratio is zero for $k_\lambda = 10^4$, and grows to ≈ 4 for $k_\lambda = 10$. For comparison, the most stable configurations presented in [88] that were created by Swap Monte Carlo feature a relative stress drop of ≈ 3, i.e. it is smaller by roughly 25% compared to the relative stress drop found in our most stable glasses. This difference establishes that our glassy samples’ mechanical stability is similar compared to that of the Swap-Monte-Carlo-generated glasses. We emphasize here that the computational bottleneck in this numerical experiment is the deformation simulation, which takes roughly an order of magnitude more computation time compared to the preparation of our glassy samples of 256,000 particles. We further note that the relative magnitude of the stress drop across the shear-banding event increases the most dramatically between $k_\lambda = 10^3$ and $k_\lambda = 10^2$, and saturates upon decreasing $k_\lambda$ from $10^2$ to $10$, consistent with the trend we have observed for elastic properties (reported in Fig. 2.4), indicating a possible relation between stability and elasticity.

To assess the degree of plastic deformation occurring along the elasto-plastic transients, we have performed single shear cycles on systems of 16,000 particles; we deformed our glasses using the same athermal quasistatic scheme (described in Appendix C.2), up to various maximal strain values $\gamma_{\text{max}}$, and back to zero strain, as shown in Fig. 2.8. Interestingly, we find that at intermediate $k_\lambda$ of $10^2$ and $3 \times 10^2$, plastic events take place before the occurrence of the macroscopic shear band; however, upon reversal of the strain, the system appears to nearly return to its original, undeformed zero-stress state, see for example Fig. 2.8b. This behavior has been termed ‘partial irreversibility’ in [119], where similar findings for well-annealed hard sphere glasses were reported. Upon further decreasing $k_\lambda$ to $10^2$, very few plastic events take place before the macroscopic shear band occurs.

In Fig. 2.9 we report the sample-to-sample mean energy density dissipated in a shear cycle, made dimensionless by rescaling by the undeformed solids’ shear modulus, namely $G^{-1} \int_{\gamma_{\text{max}}}^{\gamma} \sigma \, d\gamma$. Averages were taken over 100 independent realizations for each $k_\lambda$-ensemble.
2.5. Scaling argument for the gap in the density of quasi-localised excitations

Consistent with the depletion of quasi-localised modes in the small \( k_\lambda \) glasses, we observe a remarkably small degree of dissipation up to the macroscopic shear-banding event in those samples.

\[
G \left \{ \gamma \right \} = \int d\gamma \, \sigma \, d\gamma \\
G \left \{ \gamma \right \} \approx 10^{-3} \quad \text{for} \quad k_\lambda = 3 \times 10^3, 10^2, 3 \times 10^3, 10^2, 3 \times 10^3
\]

\[
\gamma_{\text{max}} \approx 0.05, 0.1, 0.15
\]

**Figure 2.9** – Energy dissipated per unit volume (made dimensionless, see text) in a shear cycle of magnitude \( \gamma_{\text{max}} \), reported in linear (a) and logarithmic (b) scales.

2.5 Scaling argument for the gap in the density of quasi-localised excitations

Consider for a given \( k_\lambda \) the lowest-frequency quasi-localised modes, which appear at a frequency scale \( \omega_\Delta \). We shall argue that \( \omega_\Delta \sim 1/\sqrt{k_\lambda} \) or larger, otherwise the initial configuration would not be at a minimum of the energy function \( \mathcal{U} \) defined in Eq. (2.1). We denote by \( \tilde{M} \) the \( N(d+1) \times N(d+1) \) hessian matrix of \( \mathcal{U} \), which must be positive definite in any minimum. In the limit where \( k_\lambda \) is infinite, the spectrum of \( \tilde{M} \) is the union of the spectrum of \( M \), together with additional modes at frequencies \( \sim \sqrt{k_\lambda} \) corresponding to the “breathing” of individual particles. For finite \( k_\lambda \) the breathing modes hybridize with the usual vibrational modes, lowering the frequency of the latter. For large \( k_\lambda \) this softening can be computed straightforwardly by perturbation theory [106], and is of order \( \Delta \omega^2 \sim -\left\langle \delta f_i^2(\omega) \right\rangle_i / k_\lambda \) where \( \delta f_i(\omega) = \sum_{j \neq i} \delta \left[ \frac{\partial\phi_{ij}}{\partial \lambda_{ij}} \right](\omega) \) is the compression induced by a mode of frequency \( \omega \) on particle \( i \), and \( \langle \rangle_i \) indicates an average on all particles. In the inset of Fig. 2.5b we scatter-plot \( \left\langle \delta f_i^2(\omega) \right\rangle_i \) vs. frequency \( \omega \) of quasi-localised vibrational modes \( \dagger \) calculated in our \( k_\lambda = \infty \) glasses, to find that they are independent of frequency.

Next we use the observation [58, 100, 120] that the low-frequency of quasi-localised modes stems from the near cancellation of two terms \( \omega^2 = \omega^2_+ - \omega^2_- \). The contribution \( \omega^2_+ \) corresponds to the stretching of interactions whose characteristic stiffness is denoted \( k \) and must scale as \( \omega^2_+ \sim \left\langle \delta f_i^2(\omega) \right\rangle_i / k \), whereas \( \omega^2_- \) emerges due to pre-stress effects [121] and interactions with

\[\dagger\]We consider the lowest vibrational mode per glass in systems of \( N = 4000 \) particles, which is typically quasi-localised [54].
negative stiffnesses (usually absent in systems of purely repulsive particles). Counter-examples to this near cancellation can be found — e.g. rattlers in systems of purely repulsive particles. However (i) it can be shown to hold for modes causing the boson peak in a variety of systems [122, 123, 124, 113], and (ii) the architecture of the modes forming the boson peak at frequency $\omega_{\text{BP}}$ was found to be essentially similar to that of quasi-localised modes, with $\omega_k^2 \sim \omega_{\text{BP}}^2$ [58].

Using this result, we thus predict that $\omega_k^2 \geq \Delta \omega^2 \sim \omega_{\text{BP}}^2 (k/k_\lambda)$, a bound indeed consistent with our observation. This bound, which must hold in all the inherent structures of $\mathcal{H}$, must also hold true for the ground state of the usual potential energy $U$. As a consequence, in continuously polydisperse materials, quasi-localized modes in very low-energy glassy configurations must be gapped.

If quasi-localised modes are gapped, then other excitations including shear transformations and two-level systems with small tunnelling barriers must also be gapped, since otherwise would imply the existence of vibrational modes in the forbidden frequency range [90]. For example, using the fact that shear transformations sit near a saddle-node bifurcation, we expect the characteristic stress at which plasticity sets in to scale as $\omega_k^4 \sim \Delta^2$.

### 2.6 Summary and discussion

In this work we introduced a simple computer glass former and preparation protocol — following ideas put forward in [106] — that enables the generation of ultrastable glasses. By allowing the effective sizes of particles to fluctuate during glass formation, and freezing them thereafter, we are able to generate extremely stable glassy configurations at minimal computational cost. We demonstrated that the mechanical stability of our glasses is readily tunable by varying the stiffness $k_\lambda$ associated with the effective size DOF; and showed that it is at least comparable to the mechanical stability of glasses created using the Swap-Monte-Carlo method [88]. Structural analyses reveal that no ordering takes place in any of our glasses.

Since our ultrastable glasses are not created via a physical protocol, they may not be faithful representatives of real-world glasses. Also, their polydisperse nature, which is not a generic feature of structural glasses, is clearly key to their enhanced stability. This raises the crucial question of whether the structural and mechanical characteristics of our glasses are generic, or, conversely, that our glass-formation protocol introduces non-generic features. This resembles the open question posed in [7] of whether the absence of two-level systems in ultrastable vapor-deposited glasses is due to their increased stability (and hence, is a generic property of ultrastable glasses), or their preparation protocol.

The qualitative correspondence between the discontinuous response of bulk metallic glasses and that of our ultra-stable glasses is an encouraging item with regards to the genericity of our results. Our approach may thus help resolve which precise microstructural features of glassy solids are responsible for their mechanical stability. For example, results from our deformation simulations indicate that there should exist a critical stiffness $k_{\lambda,c}$ above which a discontinuous event nucleates, as predicted by several approaches [125, 88, 89]. In [89] the anisotropy of the problem is included, and the discontinuous event for very stable glasses
2.6. Summary and discussion

corresponds to a narrow shear band whose nucleation shares similarity with that of a fracture, a scenario that could be tested with our obtained configurations.

There is a qualitative difference between the nonphononic density of vibrational modes of glasses created with the Swap Monte Carlo algorithm and glasses created with our approach. In [57] it was shown that glasses created by Swap Monte Carlo retain gapless non-Debye spectra, featuring $D(\omega) \sim \omega^4$ even for the most deeply annealed and stable glassy samples that can be created with that approach. This stands in contrast to the spectra of our ultrastable glasses, that feature a gap for any finite $k_\lambda$.

Two possible origins of the difference between these results are: (i) glasses created with Swap Monte Carlo are quenched from a finite (although rather low) temperature, whereas our protocol produces glasses that undergo structural relaxation all the way down to zero temperature; (ii) the equivalence between Swap Monte Carlo ultrastable glasses and our ultrastable glasses is only expected in the thermodynamic limit [107, 108, 106], in which a particle in a canonical (i.e. with no external particle reservoir) Swap Monte Carlo system can assume any size within a finite support of relative width $\Delta$. However, in finite-size Swap Monte Carlo systems, a particle can only swap sizes with the $N-1$ other members of a single, particular realization of the polydispersity. This finite-size discretization, which is completely absent in our approach (our particles can assume any size), may introduce structural frustration and reduce the effectiveness of polydispersity in stabilizing the glass.

We note that the formation of a gap in the nonphononic density of vibrational modes also occurs when the degree of internal stresses is relieved by artificially reducing the magnitude of pairwise forces in model glasses [113, 100]. Interestingly, measurements of a dimensionless characterization of sample-to-sample stress fluctuations in our glassy samples (see Fig. 2.4a) also indicate a reduction of internal stresses with increasing stability.
3 Thermal origin of quasi-localised excitations in glasses

Abstract

Key aspects of glasses are controlled by the presence of excitations in which a group of particles can rearrange. Surprisingly, recent observations indicate that their density is dramatically reduced and their size decreases as the temperature of the supercooled liquid is lowered. Some theories predict these excitations to cause a gap in the spectrum of quasi-localised modes of the Hessian that grows upon cooling, while others predict a pseudo-gap $D_L(\omega) \sim \omega^\alpha$.

To unify these views and observations, we generate glassy configurations of controlled gap magnitude $\omega_c$ at temperature $T = 0$, using so-called ‘breathing’ particles, and study how such gapped states respond to thermal fluctuations. We find that (i) the gap always fills up at finite $T$ with $D_L(\omega) \approx A_4(T)\omega^4$ and $A_4 \sim \exp(-E_a/T)$ at low $T$, (ii) $E_a$ rapidly grows with $\omega_c$, in reasonable agreement with a simple scaling prediction $E_a \sim \omega_c^4$ and (iii) at larger $\omega_c$ excitations involve fewer particles, as we rationalise, and eventually become string-like. We propose an interpretation of mean-field theories of the glass transition, in which the modes beyond the gap act as an excitation reservoir, from which a pseudo-gap distribution is populated with its magnitude rapidly decreasing at lower $T$. We discuss how this picture unifies the rarefaction as well as the decreasing size of excitations upon cooling, together with a string-like relaxation occurring near the glass transition.

3.1 Introduction

A key feature of structural glasses is that groups of particles can rearrange locally between two metastable states. This motion can be triggered by quantum or thermal fluctuations, or...
mechanically by exerting an external stress or strain. Such rearrangements are associated with different excitations. At low temperature the dominant source of excitations are two-level systems (TLS) that stem from quantum tunnelling between the metastable states [9, 10, 127]. At higher temperatures, relaxation in supercooled liquids near the glass transition occurs via thermally activated events, observed to become more and more string-like upon cooling [24, 25]. Upon mechanical loading, at any temperature below the glass transition, plasticity occurs when a group of particles becomes unstable. In the potential energy landscape, this corresponds to a saddle-node bifurcation [32, 33] and leads to a rearrangement denoted ‘shear transformation’ [26]. Understanding how temperature or system preparation controls the density of these excitations remains a challenge. It is, however, a question of practical importance since: (i) the density of shear transformations controls for instance the glass brittleness [87, 88, 89], (ii) the rarefaction of activated events near the glass transition controls its fragility [128], and (iii) the density of TLS (recently observed to be almost absent in ultra-stable glasses [129, 7]) affects the decoherence in cubits [18] important for quantum computing. Finally, the possible unification of these excitations into a common description is a fundamental problem for a prospective theory of glasses.

These localised excitations should affect the low-frequency spectrum of the Hessian of the energy landscape, since groups of particles that can easily rearrange tend to have a small linear restoring force [15, 32, 90]. Indeed, in numerical glasses, such quasi-localised modes are found at low-frequencies [63]. Recently there has been a considerable effort to analyse them [52, 54, 55, 66, 58, 57]. In most glasses, it is found that in inherent structures*, the density of quasi-localised modes $D_L(\omega) \approx A_4(T)\omega^4$, with $\omega$ the frequency. Most remarkably, $A_4(T)$ is reduced by several decades as $T$ is reduced by 30% [57, 68] (a similar finding was obtained for the density of TLS [85]). Furthermore, quasi-localised modes also display a lower participation ratio at lower $T$. A unifying explanation for these facts is currently missing†. On the theoretical side, two distinct approaches have been proposed. On the one hand, the $\omega^4$ power law has been rationalised by making specific assumptions on the disorder and by assuming modes as non-interacting [79, 72], or by modelling a quench from $T = \infty$ and including interactions [90]. On the other hand, in mean-field calculations in infinite dimensions for temperatures below the mode-coupling temperature $T_c$ [3] the spectrum of the Hessian becomes gapped (excluding obvious long wave-length Goldstone modes that are always present). Below $T_c$, the gap is predicted to grow as $T$ decreases [16, 82, 83]. A gap was also predicted from real-space stability arguments in finite dimensions for continuously polydisperse particles, at very low energies and zero temperature [97]. Nevertheless, it is currently unclear if a gap truly exists in finite dimension and at finite temperature.

In this article we seek a unifying scenario for these facts and different approaches, by studying the stability of gapped spectra with respect to thermal fluctuations. Specifically, we use ‡

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*Obtained by rapidly quenching an equilibrated liquid (at initial temperature $T$) to zero temperature.
†TLS were proposed to be controlled by the so-called mosaic length scale that diverges at the Kauzmann temperature $T_K$ in mean field approaches [130]. Yet this description predicts a growing (instead of decreasing) length scale and a mild (a factor 10 at most) decrease of density of excitations upon cooling.
‡‘Breathing’ particles is an alternative version of swap algorithms in which particles of different radii are
3.2 Generating gapped glasses

in order to generate athermal ultra-stable glasses of controlled gap magnitude \( \omega_c \). Then, as sketched in fig. 3.1, we transiently reheat these glasses, with a standard molecular dynamics simulation, at a low temperature \( T_a \) for a duration \( t_a \), before quenching them back to zero temperature. Our central results are that (a) thermal fluctuations, even small, destroy the gap and we recover a density \( D_L(\omega) \approx A_4 \omega^4 \); the prefactor \( A_4(T_a, t_a) \) depends very mildly on \( t_a \) but presents an Arrhenius dependence on temperature with \( A_4 \sim \exp(-E_a/T_a) \) (in our temperature units the Boltzmann constant \( k_B = 1 \)). (b) The activation energy \( E_a \) rapidly increases with the gap magnitude \( \omega_c \). (c) We introduce a novel algorithm to decompose the rearrangements into elementary excitations, and find that they involve fewer particles for larger gap values, and eventually become string-like for our largest gap. We propose a scaling argument for their decreasing size. Overall, these results suggest to describe equilibrated liquids perturbatively as gapped states decorated by thermally activated excitations whose characteristic energy is controlled by the gap itself, leading to a contribution with \( A_4 \sim \exp(-E_a(\omega_c(T))/T) \). We discuss the implications of this picture, sketched in fig. 3.1, for the density of these various excitations, for their effect on plasticity and on low-temperature properties of glasses as well as for the glass transition.

Figure 3.1 – Schematic density of states for an equilibrated liquid at temperature \( T \). When a gapped glass is heated to a temperature \( T_a \) for a duration \( t_a \), as sketched in the inset, modes beyond the gap act as a reservoir of excitations that can be thermally activated. It fills up the gap, leading, for small \( \omega \), to a pseudo-gap \( D(\omega) \approx D_L(\omega) \approx A_4 \omega^4 \). This effect is exponentially diminished if \( \omega_c \) increases (corresponding to a decrease of \( T \) as predicted by the infinite-dimensional mean-field description near the glass transition).

3.2 Generating gapped glasses

To generate ultra-stable glasses displaying a finite gap, we follow a procedure similar to [97]. We consider ‘breathing’ particles whose individual size can vary according to an energetic cost exchanged [86].

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exchanged [86].
Chapter 3. Thermal origin of quasi-localised excitations in glasses

of characteristic stiffness $K$ (see appendix D.2). The particles interact with a repulsive potential, up to a finite cutoff radius, chosen such that the potential remains continuous up to its third derivative [76] and thus allowing for a well-defined Hessian. At a given temperature, this system is known to be thermodynamically equivalent to a system of given (and continuous) polydispersity, and can be simulated using a usual molecular dynamics (MD). Including this breathing degrees of freedom leads to a giant shortening of the equilibration time, comparable to that of swap algorithms [106, 131]. In practice, we perform MD with breathing particles for a long duration $t_p$ at a temperature $T_p(K)$, chosen such as to minimise the energy of the states eventually obtained (see appendix D.3), before quenching using a ‘FIRE’ algorithm [110] in which particles can still breathe.

The polydispersity obtained for various values of stiffness $K$ is shown in fig. 3.2(a) for $N = 8000$ particles, in three dimensions and at fixed pressure. Next, we freeze the radius of each particle, and compute the usual Hessian of the potential energy: its eigenvectors correspond to the vibrational modes of the glass, and its eigenvalues are denoted $\omega^2$ since they correspond directly to the frequencies of vibrational modes, as we take the particle mass to be unity. Showing that these states are gapped requires considerable statistics; in fact, we collect the spectra of $n = 4000$ independent realisations (see appendix D.1 for a precise statement) and average them in order to obtain the density of vibrational modes $D(\omega)$. We emphasise that for the considered small system size, quasi-localised modes are already found below the first plane waves [54].

$D(\omega)$ turns out to display a gap: there are no quasi-localised modes below a finite frequency $\omega_c$. Since we find $\omega_c$ to be even higher than the frequencies of the first plane waves for $K = (10^2, 10^3)$ we manually remove them in order to measure the density of quasi-localised modes $D_L(\omega)$, as shown in fig. 3.2(b). We extract $\omega_c$ by fitting a power law $D_L(\omega) \sim (\omega - \omega_c)^\zeta$, and obtain the values $\omega_c \approx (1.64, 1.19, 0.85, 0.65)$, for $K = (10^2, 10^3, 3 \times 10^3, 10^4)$, indicated with markers in fig. 3.2(b). Note that if we consider instead the minimal frequency observed as an estimate for $\omega_c$, our conclusions below are not affected (see appendix D.4).

Figure 3.2 – (a) Distribution of particle radii, normalised by the number density $\rho = N/\langle V \rangle$, for different values of stiffness $K$. (b) Density of quasi-localised modes displaying a finite gap $\omega_c$, in contrast to the usual pseudo-gap scaling $D_L(\omega) \sim \omega^4$ indicated with a dashed line. The gap values $\omega_c \approx (1.64, 1.19, 0.85, 0.65)$ corresponding respectively to $K = (10^2, 10^3, 3 \times 10^3, 10^4)$ are indicated using ticks, following the same color code. Physically, decreasing $K$ results to a larger gap and thus a more stable glass, and is associated to a larger polydispersity.
3.3 Filling up the gap via thermal activation

To test the robustness of gapped states to thermal fluctuations, we reheat our samples to a temperature $T_a$ and run MD simulations for a duration $t_a$, before applying an instantaneous quench to zero temperature. This procedure is sketched in fig. 3.1 (and further detailed in appendix D.2), and is entirely performed at fixed particle radii. Upon reheating, local rearrangements§ are thermally triggered (though less than 50% of the samples do rearrange at the lowest temperature that we probe¶), consequently modifying the spectrum.

In fig. 3.3(a) the low-frequency tail of $D(\omega)$ is shown for our stablest system (with $\omega_c = 1.64$) for $t_a = 500$ and varying $T_a$. Note that the acquisition of sufficient statistics required about

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§We define a rearrangement by a finite norm of the displacement field that results from reheating, see appendix D.1 for details.

¶For our system size, at $t_a = 500$ (the time scale we use later), the temperature for which we have in average one rearrangement per realisation $T^*_a (\omega_c = 1.64) \approx 0.17$, which we estimate using the fit of the Arrhenius-like behaviour below.
10^5 CPU hours. We always find that the gap is replaced by a pseudo-gap, compatible with the standard scaling:

$$D_L(\omega) \approx A_4(T_a, t_a) \omega^4.$$  \hspace{1cm} (3.1)

The prefactor $A_4$ characterises the density of quasi-localised excitations, and is extracted by fitting eq. (3.1) for $\omega < \omega_e$, where $\omega_e$ is the frequency of the first plane wave (see fig. 3.2(b)). As shown in fig. 3.3(b), $A_4$ varies immensely (by three orders of magnitude), mostly due to the variation of the temperature $T_a$, with only a mild dependence on the time $t_a$. Moreover, we show in fig. 3.3(c) that these curves can be collapsed, in the range of parameters probed, assuming the functional form $A_4(T_a, t_a) = f(t_a^4 \exp(-E_a/T_a))$ and $\gamma = 0.2$. The function $f$ is linear at small argument, supporting an Arrhenius behaviour at low temperature $T_a$ (see appendix D.4). Remarkably, this collapse indicates that for a given gap, the distribution of excitation energies is characterised by a single energy scale $E_a$ (presumably a lower cutoff, see below).

Interestingly, we find in fig. 3.3(d) that $E_a$ very strongly increases with gap magnitude $\omega_e$ (see below for a proposed explanation). The dynamical exponent $\gamma(\omega_e)$ is also shown in inset, and remains smaller than 0.2 in the entire range of initial gaps that we probe.

### 3.4 Modes beyond the gap act as an excitation reservoir

We saw that, if we start from a glass with an initially gapped density of states, thermal fluctuations will always populate this gap. To rationalise these findings, we consider the path of minimal energy connecting two states associated to one excitation, and denote by $s$ the curvilinear coordinate along it. The Taylor expansion of the energy along this path from the state 1, by definition the one of minimal energy, reads:

$$E(s) = \frac{1}{2!} \lambda_1 s^2 + \frac{1}{3!} \kappa_1 s^3 + \frac{1}{4!} \chi_1 s^4 + \mathcal{O}(s^5)$$  \hspace{1cm} (3.2)

which is a double-well, with a curvature $\lambda_1 \approx \omega_2^2$ around the minima in state 1.

In that formalism, starting from a gapped glass correspond to having a distribution $P(\lambda_1, \kappa_1, \chi_1)$ strictly zero at $\lambda_1 < \omega_2^2$ and smooth above $\omega_2^2$. At finite temperature the gap is populated by thermal activation towards a state 2 with a smaller frequency $\omega_2 \approx \sqrt{\lambda_2}$, which corresponds to a transition in an asymmetric double-well (as illustrated in Fig. 3.1). From eq. (3.2) it is straightforward to obtain the expansion from state 2, and the transformation $(\lambda_2, \kappa_2, \chi_2) = g(\lambda_1, \kappa_1, \chi_1)$. The joint distribution follows $P(\lambda_2, \kappa_2, \chi_2) = |g'(\lambda_2, \kappa_2, \chi_2)|P(\lambda_1, \kappa_1, \chi_1)$ where the absolute value of the determinant of the Jacobian $|g'(\lambda_2, \kappa_2, \chi_2)| \sim \lambda_2$ for small $\lambda_2$ (see appendix D.5). Owing to the smoothness of $P(\lambda_1, \kappa_1, \chi_1)$ for $\lambda_1 \gtrsim \omega_2^2$, for small $\lambda_2$ one has $P(\lambda_2, \kappa_2, \chi_2) \sim \lambda_2$ or equivalently $P(\omega_2, \kappa_2, \chi_2) \sim \lambda_2 d\lambda_2/da \sim \omega_2^3$. After integrating on $\kappa_2$ and $\chi_2$ one gets $D_L(\omega_2) \sim \omega_3^3$. See [72] for a more general argument along the same line. Thus one expects to observe a pseudo-gap following thermally activated excitations. One effect will deplete the spectrum even further: in the case of a cubic pseudo-gap, the low-frequency spectrum is dominated by states 2 very close to a saddle node bifurcation (at the spinodal). However,
3.5. Effects of a thermally filled-up gap on physical properties

Once interactions among excitations are taken into account, configurations with such a large density of states near saddle node bifurcation can be shown to be unstable and display avalanche-type events, i.e. where the relaxation of one excitation can destabilise others in turn [90]. This effect will increase the pseudo-gap exponent to values larger than three**.

As far as the kinetics is concerned, the time scale \( t_a \) on which an excitation equilibrates depends on the energy barrier \( \Delta E \) to go from state 1 to 2. It will occur (neglecting prefactors) when \( t_a \gg t_a^* \sim \exp(\Delta E / T) \), i.e. its first-passage time. For much larger time scales, the probability of being in the excited states follows a Boltzmann factor \( \exp(-E_{12} / T) \), i.e. its first-passage time. For much larger time scales, the probability of being in the excited states follows a Boltzmann factor \( \exp(-E_{12} / T) \), i.e. its first-passage time. For much larger time scales, the probability of being in the excited states follows a Boltzmann factor \( \exp(-E_{12} / T) \), i.e. its first-passage time. For much larger time scales, the probability of being in the excited states follows a Boltzmann factor \( \exp(-E_{12} / T) \), i.e. its first-passage time.

For a given gap magnitude \( \omega_c \), we expect to find a lower cutoff on the distribution of barriers \( \Delta E \) (with the typical energy difference \( E_{12} \) of the associated excitations being of the same order of magnitude). Consider for instance a symmetric double-well in the energy landscape and expand its energy around the maximum: \( E(s) = -\frac{1}{2} \lambda s^2 + \frac{1}{4} \chi s^4 \). It is straightforward to show that in each minimum the frequency of the soft mode scales as \( \sqrt{\lambda} \), allowing us to identify for the softest excitations \( \lambda \sim \omega_c^2 \). Likewise in this example the barrier for the double-well follows \( \Delta E \sim \lambda^2 \sim \omega_c^4 \). This scaling holds for asymmetric double-wells as well (see Appendix E). Interestingly, our measured activation energy \( E_a \) is compatible with this power-law relation, except for the smallest gap (hence less stable glass) that we study††.

Overall, this analysis supports the scenario that modes beyond the gap act as a reservoir of excitations, with a broad distribution of barriers presenting a typical cutoff \( E_a \sim \omega_c^4 \) at low energies.

3.5 Effects of a thermally filled-up gap on physical properties

3.5.1 The softening of loading curves is proportional to \( A_4 \)

We now discuss the practical implications of the preparation dependent amplitude \( A_4(T_a, t_a) \) on the mechanical properties of the ultra-stable glass. The relationship between shear transformation and quasi-localized modes was studied in [90] for rapidly quenched glasses. More

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1Such interactions are relevant even at high temperature near the glass transition [132]. Note that when quenching the system to zero temperature after a reheating, interactions with relaxing vibrational modes may also destabilise excitations which are close to their spinodal.

2Interactions between excitations cause a pseudo-gap in the density \( P(x) \sim x^\theta \) of excitations within a force \( x \) to fail [40, 48]. Near a saddle-node bifurcation, one has \( \omega \sim x^{1/4} \) leading to \( D_L(\omega) \sim \omega^\alpha \) where \( \alpha = 3 + 4\theta \). Empirically \( \theta = 0.3 \) after a slow quench from high temperature (but it is larger for a fast quench) [90], which would lead to an exponent \( \alpha \approx 4.2 \) consistent with our measurement.

††We observed that for small gaps the assumption that all the excitations are in their energy minimum breaks down, but on the contrary for our largest gap it holds true for about 90% of excitations causing quasi-localised modes. This state of affairs is expected since for very small gaps particles can hardly breathe, and the corresponding gapped states obtained by our protocol are not extremely stable.
generally, more stably prepared systems exhibit a steeper loading curve and have a lower density of quasi-localised modes [88, 90]. Here, we show a quantitative relationship between the amplitude of quasi-localised modes $A_4$ and the effective shear modulus during loading $\mu \equiv \langle \Sigma \rangle / \epsilon$, where $\epsilon$ is the imposed shear strain and $\langle \Sigma \rangle$ is the ensemble average of the corresponding shear stress increase ‡‡. More plasticity leads to a smaller $\mu$.

We measure the stress-strain response in ultra-stable glasses using a quasi-static loading protocol (see fig. 3.4(a)). We find that the gapped glasses have the highest effective shear modulus $\mu_0 = \langle \Sigma_0 \rangle / \epsilon$ and it decreases as the gap is filled and $A_4$ increases (fig. 3.4(b)). The reduction of the effective shear modulus $\Delta \mu(A_4) \equiv \langle \Sigma_0 - \Sigma(A_4) \rangle / \epsilon$ is proportional to $A_4$ (see fig. 3.4(c)) in the range of strains $\epsilon < 0.01$ where it is strain independent.

3.5.2 TLS disappear for large gaps

Note that in this section, we show a necessary condition for TLS being not apparent, more stringent one in chapter 5.

We argue that TLS cannot be observed if a glass presents a large gap. Indeed if the tunneling amplitude is too small, on experimental timescales a single state is visited and TLS properties are not apparent [15]. It is precisely what happens when the gap is large, as barriers are then both larger and wider. To estimate this effect we follow the treatment of soft potential models [133] that solves the Schrödinger equation in potentials described by eq. (3.2). For a symmetric double-well, the tunneling time follows $\tau = \hbar \pi / \Delta_0$, where $\Delta_0$ is the splitting energy stemming from quantum tunneling (and $\hbar$ is the reduced Planck constant). $\Delta_0$ is expressed as $\Delta_0 = W \exp(-\omega_1 / \tilde{\omega})$ where $W = \hbar (\hbar \chi_1 / (96 m^2))^{1/3}$ and $\tilde{\omega} = (\hbar \chi_1 / (2 m^2))^{1/3}$ (cf. [133]), with $m$ the particle mass. Thus if $\omega_1 > \omega_c^* \equiv (\ln W / \hbar \chi_1)^{1/3} \tilde{\omega}$, TLS are not apparent. In our simulations we find that the median of $\chi_1 \approx 4.6 m \omega_D^2 / a^2$ (for our largest gap) where $a$ is the inter-particle distance and $\omega_D$ is the Debye frequency (see appendix D.6 for details). Taking estimates in amorphous silicon where $\omega_D \approx k_B 530K / \hbar$ [134], we get $W \approx 0.03 \hbar \omega_D$ and

‡‡Shear stress is measured relative to the initial value at $\epsilon = 0$. 

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3.6 Rearrangements involve fewer particles and become string-like at large gaps

ω₀ ≈ 0.1ω_D. Considering the experimentally accessible time scale to be of order τ ≈ 100s, at last we estimate ω∗_c ≈ 0.3ω_D. It is of the order of magnitude of our largest gap ω_c ≈ 0.1ω_D.

Suppressing TLS altogether would thus be accomplished by preparing sufficiently stable glasses so as to get ω_c > ω∗_c. These considerations stay valid even when thermal activation populates the gap and A_4 becomes finite, because quasi-localised modes with low-frequency correspond then to quite asymmetric wells whose barrier height and width (and therefore tunneling amplitude) is still comparable to the estimate above. The presence of a large underlying, thermally populated, gap of quasi-localised modes in ultrastable glasses thus offers an explanation for their lack of TLS [129, 7].

3.6 Rearrangements involve fewer particles and become string-like at large gaps

We introduce a novel algorithm to decompose the displacement field of a rearrangement into several elementary excitations, which is needed to study how their geometry depends on the gap magnitude. Given a displacement field (induced, in our case, by the thermal cycle), we first consider the particle with maximal displacement, and draw a sphere of radius ˜R around it. Beyond this sphere, all the particle displacements are set to zero (i.e. these particles are set back to their initial position in the gapped state), whereas within the sphere the displacements are preserved. Next, we perform with that initial condition a steepest descent of the interaction energy. We find that if ˜R is small, all displacements go back to zero, whereas if ˜R is large, they do not. We consider the smallest ˜R of the latter case, and the displacement field obtained at the end of the corresponding gradient descent defines our first elementary excitation.

Next, we subtract this obtained displacement field from the full one, and repeat the entire procedure recursively until no more excitations are found (see appendix D.7 for details and visual examples).

Given an individual excitation of displacement field {δ⃗r_i}, we compute, from its associated participation ratio, an estimate of the number of particles involved in this excitation NP_r ≡ [Σ_i ||δ⃗r_i||^2]^2 / Σ_i ||δ⃗r_i||^4. For each gap magnitude ω_c, we find about 5000 such excitations and report the mean and the median of this observable in fig. 3.5(a). We find that the typical number of particles involved in one excitation decreases as ω_c increases. We propose the following rationalisation. The length scale of quasi-localised modes was found to be proportional to the characteristic length scale entering the response to a local dipole [58], as proposed based on a variational arguments in [135]. The length scale ℓ_c entering the dipolar response was observed to decrease as the system moves away from a marginally stable phase and enters a gapped solid phase as ℓ_c ∼ 1/√ω_c [136]. The volume of the corresponding mode was shown to go as ℓ_c^2 (independent of the number of dimensions) for elastic networks of springs at rest [136, 135]. Taken together, these results correspond to a number of particles involved in an excitation that decreases with increasing gap as NP_r ∼ 1/ω_c. As shown in the inset of fig. 3.5(a), this is in reasonable agreement with our observations.

A complementary observable for the geometry is the maximum displacement max_i(||δ⃗r_i||) for
Chapter 3. Thermal origin of quasi-localised excitations in glasses

a given excitation, whose mean and median values for all excitations at a given \( \omega_c \) are shown in fig. 3.5(b). Interestingly, this maximum displacement increases with the gap, and becomes close to the small particle diameter equal to \( d_0^* \).

A direct visualisation of the excitation fields reveals a (presumably related) interesting phenomenon: for our largest gap, the displacements are string-like with several particles exchanging positions, as shown in fig. 3.5(c), whereas for smaller gaps they are much more compact and no permutations occur. To quantify this effect, we follow the glass transition literature \cite{24} and measure the distinct part of the Van Hove correlation:

\[
G_d(\vec{r}, t) \equiv \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta(\vec{r} - \vec{r}_j(t) + \vec{r}_i(0)) \right\rangle, \quad (3.3)
\]

where the average is made on all the observed elementary excitations at some given \( \omega_c \). It is plotted for our stabllest system in fig. 3.5(e) after radially averaging. The key observation is the presence of a very sharp peak around \( r = 0 \), which can only arise from particles replacing each other. Interestingly, if we condition our definition of the Van Hove correlation to large or small particles only, we find that the peak only persists for small particles (in red in fig. 3.5(e)).

Strings thus correspond to smaller particles navigating in an environment of larger ones.

Next we integrate the peak around \( r = 0 \) to quantify the number of permuting particles averaged on all elementary excitations:

\[
\langle n_p \rangle = \left\langle N \int_0^{r_c} G_d(r, t_0) 4\pi r^2 dr \right\rangle, \quad (3.4)
\]

where \( r_c \) is a cutoff that is tuned. We observe that permutations are essentially absent except for the largest considered gap, see fig. 3.5(f).

3.7 Discussion

In summary, we have argued that in gapped glasses, modes beyond the gap act as an excitation reservoir for thermal activation. This effect always destroys the gap and leads to a density of quasi-localised modes \( D_L(\omega) \approx A_4(T) \omega^4 \). At low temperatures, we found that \( A_4 \sim \exp(-E_a(\omega_c)/T) \) where the typical energy scale \( E_a(\omega_c) \) is a rapidly increasing function of \( \omega_c \). A simple scaling prediction gives \( E_a \sim \omega_c^4 \), in good agreement with our observations, except for the smallest gap value that we explore. Finally, we observed that as the gap increases, excitations involve fewer and fewer particles and become more and more string-like. The growing length scale of the excitations as \( \omega_c \to 0 \) is consistent with the previously identified growing length characterising the elastic response of an amorphous solid near a macroscopic elastic instability \cite{136}.

Although our observations were made in ultra-stable states obtained by a specific protocol\$\$,\$\$,

\$\$In general to create gapped glasses one needs to use a gradient descent method using swap or equivalently breathing particles up to zero temperature. If instead one uses MD with the normal dynamics to quench from a finite temperature, the gap of magnitude \( \omega_c \) will be filled by excitations
our arguments on this reservoir effect are much more general. Assuming that this effect is at play in supercooled liquids ties together several unexplained observations, as we now discuss. 

Reinterpreting mean-field descriptions of glasses: Goldstein [84] proposed early on that the glass transition takes place near some temperature $T_c$ below which most normal modes become stable. Such an enhanced stability is consistent with the overall elastic stiffening upon cooling apparent in the bulk [23] or local [66] elastic moduli in fragile supercooled liquids. Theoretically, this view is consistent with mean-field models of the glass transition in infinite dimensions – that are closely related to Mode-Coupling Theory – [16, 82], in which the spectrum of the Hessian becomes stable and opens a gap with $\omega_c^2 \sim (T_c - T)$ [83]. Our work suggests a natural way to extend this picture to finite dimensions as sketched in fig. 3.1: the gap is decorated by excitations stemming from the reservoir of modes with $\omega \geq \omega_c$. In this approach (i) the excitation density strongly decreases with temperature: away from $T_c$ in the deeply supercooled regime, it should be proportional to $\exp(-E_a(\omega_c(T))/T)$ and (ii) as $T$ decreases, $\omega_c$ increases and excitations are less and less extended. Point (i) offers an explanation for the very rapid decay upon cooling of $A_4(T)$ [57, 68], TLS density [137] and shear transformations [88, 119] observed in ultra-stable supercooled liquids. Point (ii) is consistent with the result that TLS [137] and quasi-localised modes [57, 68] present a lower participation ratio upon cooling (such changes of geometry may lead to additional effects on their density).

Glass transition: The mean-field proposal that supercooled liquids present an effective gap growing upon cooling, leading to a rarefaction of thermally accessible excitations, is consistent with the observation that rearrangements become string-like with more and more particles exchanging positions upon cooling [24, 25] – since we find that excitations at large gap are precisely like that. In our view, why elementary excitations display such a geometry at large gap is yet to be explained.

At our lowest temperatures, only one or a few strings get activated, which can only lead to a very partial relaxation of the system. Isolated strings thus belong to the class of $\beta$-relaxation in supercooled liquids, as shown in [25], using normal dynamics, for model metallic glasses (molecular and covalent liquids may certainly present other $\beta$-relaxation mechanisms governed by the local chemistry, such as dangling bonds). Yet strings may also contribute the $\alpha$-relaxation of liquids if they are present in sufficient density, at least for the continuously polydisperse ones receiving much attention currently. Indeed they allow for the exchange of particles with distinct radii. Such swap moves are now known to relax the system with great efficiency, so the dynamics should not be slower than the time scale to naturally operate these swaps [140, 141]. The rapid increase of their characteristic low-energy cutoff $E_a$ with growing gap would then contribute to the fragility of liquids.

¶¶See [68] for a discussion on quasi-localised modes. Concerning TLS, a smaller participation ratio suggests a higher tunnelling amplitude, which may in turn affect the TLS density.

***It was argued within RFOT that strings would exist in some temperature range [138, 139]. Yet, this analysis is based on the “library of states” picture that describes only rough barriers consisting of many intermediary ones (that must exist between each state of the library). This description thus cannot apply to the elementary excitations displaying a single barrier studied here. In our view, a description of strings should also explain why particles exchange positions.
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Note that such views in which activation deep in the supercooled liquid phase is controlled by $T_c$, contrasts with the usual interpretation of mean-field results in which activation is controlled by an entropy crisis occurring at a lower temperature $T_K$ (the Kauzmann temperature) [16, 82]. The latter is in our opinion ruled out in poly-disperse systems by the recent observation that changes of kinetic rules (such as allowing for swap moves [86]) immensely affect the location of the glass transition, while leaving intact thermodynamic properties [140]. Changes of kinetic rules, however, affect the location of the mode coupling temperature $T_c$ [141, 106], thus pictures of activation based on that temperature are consistent with the observations of swap algorithms.

Effects of rare fluctuations: We have shown that a gap in the density quasi-localised modes cannot exist in finite dimension at finite temperature, due to the thermal activation of their associated excitations. We expect that at least another effect will enter in finite dimension to fill up the gap. In electronic systems that present impurities, the density of states does not vanish in the range of energies where the pure system would, due to rare regions where many impurities are present. This effect leads to the so-called “Lifshitz tail” in the electronic density [142]. In glasses, we expect that aspects of the structure controlling stability, such as coordination and pressure [121, 122], will also fluctuate and lead to rare weaker regions in the materials (we do not see this effect in our breathing particles, whose preparation may lead to an unusually homogeneous material). Such fluctuations will need to be larger and larger as the gap grows to contribute to low-frequency quasi-localised modes, and therefore less likely, leading to a rapidly decaying density of quasi-localised modes with growing gap. These atypical rare regions may have little effect for plasticity or structural relaxation near the glass transition, but may be important in affecting the density of TLS. It would thus be interesting in the future to study glasses of controlled inhomogeneity to separate rare fluctuations in the structural disorder from the ‘excitations reservoir’ effect introduced here.
3.7. Discussion

Figure 3.5 – (a) Mean (dashed black) and median (green) of the number of particles $N_{P_r}$ involved in an individual excitation vs $\omega_c$ at $t_a = 500$ (at the lowest temperature we probe for each gap). The error bars stand for the standard deviation of $N_{P_r}$ which indicates that the distribution of $N_{P_r}$ is broader for smaller $\omega_c$. (b) Mean (dashed black) and median (green) of the displacement norm of the most mobile particle in an excitation, as a function of $\omega_c$. $d_0^*$ is the most frequent diameter of the smaller particles ($d_0^* = \{0.738, 0.918, 0.963, 0.988\}$ for the different $\omega_c$). (c)-(d) Thermally induced rearrangement, respectively for our largest ($\omega_c = 1.64$) and smallest ($\omega_c = 0.65$) gaps, projected on the $xy$ plane. (e) Ensemble and radially averaged (on all observed excitations) Van Hove correlation function $G_d(r, t_a)$ computed for all (black), only small (red) or only large (blue) particles for $\omega_c = 1.64$. The peak around $r = 0$ corresponds to permutations of particles. The black and red curves overlap, indicating that permutations only occur on small particles. (f) Average number of permutations $\langle n_p \rangle$ vs $\omega_c$, for two different cutoff distances $r_c/d_0^* = \{0.025, 0.05\}$ (dashed and solid, respectively).
4 Alternative cause for the local excitations in structural glasses

In chapter 3, we have considered glasses prepared through the ‘breathing’ particles method, which allows for the preparation of gapped glasses, and numerically confirm our theoretical argument that gap cannot exist in real glasses at finite temperature, due to the activation of the “reservoir” of modes beyond the gap.

Yet, it is unclear if this effect is dominant contribution to $A_4$ in realistically prepared glasses, and if the geometry of excitations is similar to what we have observed in gapped glasses. In this chapter, preliminary results on the local excitations are presented for glasses obtained by an instantaneous regular quench from equilibrated configurations at low temperature $T_p$ (taken from [68]) obtained by the SWAP Monte Carlo method (see the detail of the model in E.1).

Our central results are: (i) Rearrangements in these glasses also become string-like when the glass becomes more stable. (ii) For small $T_p$, slow annealing does not affect $A_4$ in these glasses. It contrasts with gapped glasses cycled in temperature, since in that case slow annealing can bring back the modes into the reservoir. It suggests that at low $T_p$, the reservoir effects is not the c one controlling $A_4$. (iii) We propose that the dominant effect is that of spatial fluctuations, which must always exist in finite dimensions and blur the gap. A similar effect is also found in electronic system where impurities fill up the low energy spectrum of electrons, which is so-called “Lifshitz tail” in the electronic density [142]. In this view, a glass is akin to a Swiss cheese where holes are soft regions (rarer and rarer as the glass becomes more stable overall) where soft quasi-localised modes lie. We support this view with observations showing that soft QLM can come in groups localised in the same region of space. (iv) We test the idea that these soft regions are induced by rare fluctuations of key quantities controlling stability, such as coordination and pressure. Our results indicate a clear correlation. Yet, more needs to be done to characterise the geometry of these rare regions. It appears necessary to later estimate how their density depends on the overall stability of the system.

**Method:** To find the local rearrangements, we perform temperature cycles as we did in chapter 3 (see the sketch in Fig. 3.1). In particular, normal MD simulations are applied with a short duration time of $t_a = 100$ followed by an instantaneous quench where the conjugate gradient method is used. The system volume is fixed during the entire process. Through
comparing the displacement fields between initial configurations and final configurations after the temperature cycles, we can check which particles have rearranged.

4.1 Rearrangements become more string-like at lower $T_p$

In chapter 3, we found that local rearrangements become more string-like in large gapped glasses. Very interestingly, in gapless glasses (obtained by a regular quench with a quite different polydispersity), we still find the string-like rearrangements, see Fig. 4.1 (a) and (b). Several particles exchange their positions and exhibit line-like (Fig. 4.1 (a)) or loop-like (Fig. 4.1 (b)) displacement fields. To quantify this effect, we use the distinct part of the Van Hove correlation as discussed in Chapter 3 (see Eq. 3.3) and is plotted for $T_p = 0.3, 0.35, \text{ and } 0.4$ corresponding to Fig.4.1 (d), (e), and (f). The sharp peaks around $r = 0$ at $T_p = 0.3$ and $0.35$ indicate the string-like rearrangements. The magnitude of the peak decreases with increasing $T_p$ from Fig.4.1(d) to (f).

In Fig.4.1(c), we show that rearrangements become more localised with the stability of glasses increasing (decreasing $T_p$) [85], suggesting that string-like rearrangements become more. Inset of Fig.4.1(c) shows a very localised rearrangement where only one particle is significantly rearranged.

Note that the reheating temperature $T_a$ for a given duration $t_a$ at each $T_p$ determines the percentage of string-like rearrangements. We use $\langle n_p(r_c) \rangle$ as used in chapter 3 (see Eq. 3.4), which indicates the number of permuting particle of each rearrangement (averaged on all local rearrangements) when $r_c$ is small, to describe the percentage of string-like rearrangements. Here we let $r_c = 0.025d_0$ and study $\langle n_p \rangle$ by varying the number of rearrangements for each particle. $e_p = n_r/(N \ast N_s)$, where $n_r$ is the number of rearrangements and $N_s$ the number of samples. Notice that $e_p$ does not depend on $N$ and $N_s$, which can help us compare $\langle n_p \rangle$ (or other quantities) in different systems. $e_p$ is determined by $T_a$, we can thus tune it to generate different values of $e_p$ at each $T_p$.

In Fig.4.2, $\langle n_p \rangle$ increases with increasing $e_p$ at each $T_p$ except for $T_p = 0.4$ where string-like rearrangements are absent in this small $e_p$ range. This implies that with $T_a$ increasing the percentage of the string-like rearrangements become larger. More interestingly, for a given $e_p$, $\langle n_p \rangle$ increases when $T_p$ decreases. It shows that rearrangements become string-like in more stable glasses. We also plot $\langle n_p \rangle$ for the largest gapped glasses (the black curve) obtained in chapter 3. (The notation of ‘breathing’ corresponds to the largest gapped glasses obtained in chapter 3, same as below.) It is close to the curve with $T_p = 0.35$, suggesting that they have a similar level of the stability.

4.2 $A_4$ weakly depends on the annealing process at low $T_p$

In chapter 3, we showed that the power law tail of QLMs stems from thermal fluctuations that causes a group of particles to jump from the reservoir (deep minimum) to a shallow minimum whose vibrational frequency is low so that the gap is filled up (see the sketch 3.1). In those
4.2. $A_4$ weakly depends on the annealing process at low $T_p$

Figure 4.1 – Two string-like rearrangements (a) and (b) projected on x-y plane shown at $T_p = 0.3$ (lowest $T_p$ we have) obtained by the temperature cycles with the reheating temperature $T_a = 0.5$ and duration $t_a = 100$. $P_r$ is the participation ratio. $N \ast P_r$ indicates how many particles are involved. (c) The median of $NP_r$ as a function of $T_p$. A very localised rearrangement at $T_p = 0.3$ (inset of (b)). $e_p \approx 1 \times 10^{-5}, 1 \times 10^{-5}, 1 \times 10^{-5}, 1 \times 10^{-5}, 6 \times 10^{-6}, 1 \times 10^{-6},$ and $2 \times 10^{-6}$ from low to high $T_p$. (d)-(f) are the ensemble and radially averaged (on all observed local rearrangements) Van Hove correlation functions at three different $T_p$. Specifically, there are 209, 513, and 1411 local rearrangements found in 10,000 samples at $T_p = 0.3, 0.35$ and 0.4. $d_0$ is the most frequent diameter of particles. The black lines are guides to the eye.

glasses, the annealing will dramatically influence $A_4$ since a slow annealing will bring back the particles into the reservoir.

In this section, we check how the quench rate influences $A_4$, the prefactor of density of QLMs $D_L(\omega) = A_4 \omega^4$. In particular, we quench (regular dynamics) from the initial equilibrated configurations at $T_p = 0.3$ and 0.4 with three different quench rates $\dot{T} = \infty, 10^{-1},$ and $10^{-3}$ to zero temperature to check whether the quench rate strongly influences $A_4$. As shown in Fig. 4.3(a), $A_4$ at $T_p = 0.3$ and 0.4 quite weakly depends on the quench rate. Notice that the mode-coupling temperature $T_c \approx 0.8$ that is above $T_p$ that we study here. At $T_p = 0.3$, we even can barely distinguish the changes at different quench rates.

As a comparison, $A_4$ at two different quench rates in gapped glasses after temperature cycles are shown in 4.3 (b). The change of $A_4$ is much bigger than that in Fig. 4.3(a). The reason is that in gapped glasses, the slow annealing will make particles go back to the deep minima whose frequencies are large. It reduces the density of soft modes so that $A_4$ decreases.

Hence, the weak dependence of $A_4$ on the quench rates at low $T_p$ implies that the effect
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Figure 4.2 – The averaged number of permuting particle of each rearrangement \( \langle n_p \rangle \) varies by \( \varepsilon_p \) at different \( T_p \). Black curve indicates \( \langle n_p \rangle \) for the largest gapped glasses obtained in chapter 3. From the inset shown in the log-log scaling, we can see that string-like rearrangements at \( T_p = 0.4 \) are absent.

of the thermal fluctuations is tiny. In other word, the origin of gapless at low \( T_p \) is not mainly from the thermal fluctuation effect.

Figure 4.3 – (a) The density of QLMs at \( T_p = 0.3 \) and 0.4 with three different quench rates. (b) The density of QLMs for gapped glasses with two different quench rates after reheating them as indicated in legend. At low frequency \( D(\omega) = D_L(\omega) = A_4 \omega^4 \) in a small system size. \( \dot{T} = \infty \) corresponds to the instantaneous quench where the conjugate gradient method is used. The black dashed lines are the fit of \( A_4 \omega^4 \) at low \( \omega \) by fixing the exponent to extract \( A_4 \) as we did in chapter 3. At \( T_p = 0.4 \), \( A_4 \) increase by 50% from \( \dot{T} = \infty \) to \( \dot{T} = 10^{-3} \). This increase is less than that in (b) where \( A_4 \) increases by a factor 2. At \( T_p = 0.3 \), the change of \( A_4 \) is tiny compared to the change at \( T_p = 0.4 \) and in (b). 10,000 samples with \( N = 2000 \) at these two \( T_p \) are considered in (a) and 4000 samples with \( N = 8000 \) considered in (b).
4.3 **One weak region can be associated with several QLMs**

Spatial fluctuations would lead to the weak regions or soft spots where particles can easily rearrange. The directions of these local rearrangements would have big overlaps with the QLMs. In this section we will show that one weak region can be associated with several QLMs, suggesting the view that QLMs are caused by fluctuations in disorder.

To do so, we look at the overlaps between the local rearrangements and the normal modes through a local density function. For a given normalised local rearrangement \( \vec{\delta}R \), there corresponds an eigen mode \( \vec{\psi}^{(r)} \) with whom the overlap is biggest. To see whether there exist other localised modes that are associated with \( \vec{\delta}R \), we define a cumulative local density per particle \( C_i(\omega^*) \) without considering the mode \( \vec{\psi}^{(r)} \):

\[
C_i(\omega^*) = \sum_{\omega_l < \omega^*} \left( \vec{\psi}_i^{(l)} \right)^2
\]

where \( i \) is the label of particle indicating its position, and \( \omega^* \) is the tunable upper bound frequency. Here we sum the magnitude of eigen modes on particle \( i \) with their frequencies below \( \omega^* \). \( C_i \) implies the local density of the normal modes. \( C_i \) will be large on the spatial region where several QLMs present. Then we calculate the average of \( (\vec{\delta}R_i)^2 \) weighted by \( C_i \),

\[
C_R = \sum_i C_i(\vec{\delta}R_i)^2 = \sum_{\omega_l < \omega^*} \sum_i \left( \vec{\psi}_i^{(l)} \right)^2 (\vec{\delta}R_i)^2
\]

If \( \vec{\psi}^{(l)} \), excluding \( \vec{\psi}^{(r)} \), are all plane waves which have a magnitude \( 1/\sqrt{N} \) on each particle, then \( C_R = \langle C_i \rangle = \frac{1}{N} \sum_{\omega_l < \omega^*} \). It justifies to take \( \langle C_i \rangle \) as a reference. If \( \vec{\psi}^{(l)} \) are all localised on the other particles (other regions) compared to \( \vec{\delta}R \), then \( C_R < \langle C_i \rangle \). So, if there exist other modes that are overlapping with \( \vec{\delta}R \), then \( C_R > \langle C_i \rangle \). In Fig. 4.4, we show \( C_R \) v.s \( \langle C_i \rangle \) where each dot represents a rearrangement. We find that for two different \( \omega^* \), in most cases \( C_R > \langle C_i \rangle \), which supports the idea that several QLMs can be localised on the same spatial region.

4.4 **Local pressure and coordination**

To study the cause of these QLMs, we consider structural fluctuations of pressure and coordination of each particle. The local pressure on the \( i \)th particle is defined by \( p_i \equiv \frac{1}{6} \sum_{j \neq i} f_{ij} r_{ij} \) where \( f_{ij} \) is the radial force between two interacting particles \( i \) and \( j \) with the soft repulsive interaction (see the detail in E.1) and \( r_{ij} \) is their distance [35]. The local coordination \( z_i \) is defined by the local first coordination number: \( z_i = \int_0^{r_c} \sum_{j \neq i} \delta (r_{ij}) dr \) where \( r_c \) is the first minimum of the radial distribution function \( g(r) \). (See the inset of Fig. 4.5 (b) *.)

From Fig. 4.5, we find that the probability distribution of the local pressure (local coordination) in gapless glasses (prepared by regular dynamics) is broader than that in gapped glasses. This indicates that these gapless glasses, in terms of their local structures, are more

*For 'breathing' particles, the first coordination is chosen at the minimum of \( g(r) \) for bigger particles. We do not count the particles in \( z_i \) if they do not interact with the particle \( i \).
Figure 4.4 – $C_R$ v.s. $\langle C_i \rangle$ at two cutoff frequencies $\omega^*$ for three temperatures $T_p$. $e_p \approx 6 \times 10^{-5}$, $3 \times 10^{-5}$, and $6 \times 10^{-5}$ corresponding to $T_p = 0.3$, $0.4$, and $0.5$, respectively. $\omega^* = 2$ is about the frequency of the first plane waves. $\omega^* = 3$ is chosen randomly. Both choices are to see whether $C_R > \langle C_i \rangle$.

Figure 4.5 – The probability distribution of local pressure (a) and local coordination (b) at $T_p = 0.3$ and $0.55$ and for ‘breathing’ particles. $\bar{p}_1$ is the average pressure for each preparation. The inset of (b) shows the cutoff of $r_c$ to calculate the first coordination. $d_0$ is the most frequent distance of the neighbouring particles.

inhomogeneous than the gapped glasses. The quantitative distribution of $P(r)$ and $P(z)$ are model dependent. Its slope at low pressure in gapped glasses is steeper shown in Fig. 4.5 (a) with log-log scaling, which indicates a narrower distributed $P(p)$. For these gapless glasses, at small $p$ (or $z$) $P(p)$ (or $P(z)$) is larger at high $T_p$. This is consistent with the observation that
4.4. Local pressure and coordination

the density of QLMs decreases with lowering $T_P$.

Figure 4.6 – Distribution of pressure and coordination for the rearranging particles. Here 'displaced' means that the particles taken into account are selected by $NP_r$ largest displaced particles of each rearrangement. 'max dis' means the largest displaced particle. Open solid curves stand for the pressure and coordination for all particles (already shown in Fig 4.5) displayed here for comparison. $e_p \approx 2 \times 10^{-5}$ at $T_a = 0.55$ and $1 \times 10^{-5}$ at $T_a = 0.3$ (in same order of magnitude).

We now verify that the easily local rearranging particles have small pressure and coordination. To do that, we show the probability distribution of pressure and coordination for the rearranging particles in Fig. 4.6 (a) and (b) indicated by dashed curves with the notation 'displaced'. Open solid curves stand for the pressure and coordination for all particles (already shown in Fig 4.5) displayed here for comparison. Compared to the averaged values of pressure and coordination for all particles ($\bar{p}/\bar{p}_1 = 1$ and $\bar{z}_1 = 13$), particles undergoing rearrangements are at small pressure and coordination. Here the particles taken into account are selected by $NP_r$ largest displaced particles of each rearrangement. At $T_P = 0.3$, the increase of $P(p)$ (or $P(z)$) for rearranging particles compared to that for all particles at small $p$ (or $z$) is larger than the increase at $T_P = 0.55$. This implies that at lower $T_P$, the local rearranging particles have the bigger difference than their surrounding rigid particles.

We also show the distribution of local pressure and coordination for the largest displaced particle of each rearrangement denoted by the filled solid curves in Fig. 4.6. The distribution of coordination for these largest particles at small $z$ is higher than that for the rearranging ones. It would be interesting to study the local environments of these largest displaced particles and examine their respective pair forces $f_{ij}$ or pressure contributions $f_{ij} r_{ij}$.

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$^\dagger A_4$ at $T_P = 0.55$ is about 600 times larger than it at $T = 0.3$. See $D_L(\omega)$ in Appendix E.2.
5 The connection between the density of TLS and density of QLMs

TLS are believed to control the low temperature properties of glasses for a long time, and their density is found to be nearly independent of their chemical compositions [4]. However, in recent experiments it is found that glasses prepared by vapour deposition exhibit a specific heat proportional to $T^3$ below 1K, instead of the common $T$ scaling. It implies that the density of TLS, $n_0$, can decrease significantly in ultrastable glasses [7, 20]. This significant decrease in $n_0$ is supported by the latest numerical simulation that $n_0$ decreases around by a factor of 100 times in ultrastable glasses compared to poorly prepared glasses [85]. Meanwhile, it is found in numerics that $A_4$ - the prefactor of density of QLMs -, also dramatically decreases by several hundreds of times [85]. Currently the relationship between $A_4$ and $n_0$ is unclear.

In this chapter, I argue that $n_0$ is proportional to $A_4$ and to the fraction $f_{\omega_0}$ of double-wells at same characteristic frequency $\omega_0$. This argument is based on the following reasonable assumptions. Following soft-potential models, I assume that each DWP can be described by a fourth order polynomial potential along the reaction coordinate for a given system. I further make the approximation that its quartic coefficient is a constant, as supported by the numerical observation that it is narrowly distributed [54]. I then use the fact that TLS are dominated by the near equal double-well potentials (DWP) with a typical splitting energy $E$ of order $k_B T$ at low temperature [127]. For these near equal DWP, $n_0$ is dominated by $E \sim \Delta_0$ where $\Delta_0$ is the tunnelling element in the WKB approximation [10, 9]. Since $\Delta_0$ exponentially decays with the frequency $\omega$ of DWP, where $m\omega^2$ ($m$ is the corresponding mass of the particle) is the curvature of the DWP at the minimum, there exists a typical frequency $\omega_0$ corresponding to $E$. Hence, TLS are dominated by nearly symmetric DWP with a characteristic frequency $\omega_0$. The density of TLS, $n_0$, is thus proportional to the density of these DWP. The latter is proportional to $D_L(\omega_0)$. If I further assume that $D_L(\omega_0) = A_4\omega_0^4$ still holds, then I obtain that $n_0$ has a factor $A_4$.

Based on this argument, I estimate $n_0$ in glasses prepared from different parent temperature $T_p$ obtained by the SWAP Monte Carlo method. I find that $n_0$ decreases by a factor of 300 in ultrastable glasses than poorly prepared glasses with both $A_4$ and $f_{\omega_0}$ playing a significant role. More significantly, the estimations of $n_0$ are consistent with the order of magnitude of the change in $n_0$ found in amorphous silicon [129].
Chapter 5. The connection between the density of TLS and density of QLMs

5.1 Model

In this section, I will build up the connection between \( n_0 \) and \( A_4 \) based on the soft-potential models [73, 74, 75].

Following the spirit of soft-potential model, the local potential along the reaction coordinate \( s \) to the fourth order can be written by

\[
U(s) = \frac{1}{2} m \omega^2 s^2 + \frac{\kappa}{3!} s^3 + \frac{1}{4!} \chi s^4
\]  

(5.1)

where I assume the reaction coordinate to be along the QLM direction *. \( m \) is the mass of particle, \( \omega \) is the eigen frequency, and the parameter \( \chi > 0 \). Usually \( \omega, \kappa, \) and \( \chi \) are distributed for a given preparation. Due to the numerical observation that \( \chi \) is narrowly distributed [54], I set it to be a constant. The density of QLMs thus reads

\[
D_L(\omega) \equiv \int_0^\infty P(\omega, \kappa) \, d\kappa
\]

(5.2)

where \( P(\omega, \kappa) \) is the corresponding joint distribution that is introduced in the introduction 0.2 and discussed in chapter 1.

In the quantum tunnelling regime, the Double-wells potentials (DWP) are of near equal depth which indicates \( \kappa \approx \kappa_c \equiv \omega \sqrt{3m \chi} \). According to the “Standard tunnelling model” the energy splitting \( E^2 = (\delta \varepsilon)^2 + \Delta_0^2 \) [10, 9], where \( \delta \varepsilon \) is energy asymmetry (see the sketch in Fig. 2.) and

\[
\Delta_0 \approx W \exp\left(-\left(\frac{\omega}{\bar{\omega}}\right)^3\right)
\]

(5.3)

is the tunnelling contribution derived from the WKB approximation. \( W \) and \( \bar{\omega} \) are constant. They stem from the quartic potential term contribution where \( \chi \) is contained in them. Specifically, \( \bar{\omega} = (\hbar \chi / (2m^2))^{1/3} \) and \( W = \hbar (\hbar \chi / (96m^2))^{1/3} \) which are used in section 3.5.2 of the chapter 3 [133, 126].

Now I can obtain the joint distribution of \( P(E, \Delta_0) \) in the vicinity of equal wells from \( P(\omega, \kappa) \) that \( \kappa = \kappa_c + \delta \kappa \), where \( \delta \kappa \ll \kappa_c \).

\[
P(E, \Delta_0) = P(\omega, \kappa) \left| \frac{d\omega d\kappa}{dE d\Delta_0} \right| \approx P_0 \frac{E}{\Delta_0 \sqrt{E^2 - \Delta_0^2}}
\]

(5.4)

where

\[
P_0 = \frac{P(\omega, \kappa_c) \kappa_c}{18\hbar} \left( \frac{\bar{\omega}}{\omega} \right)^6
\]

(5.5)

*The above formula is same with Eq (1.1) except for that \( m \) is set to 1 as unit there.
5.1. Model

In the above calculation, I consider the leading order of \( \kappa \) around \( \kappa_c \), that \( P(\omega, \kappa) \approx P(\omega, \kappa_c) \) where \( P(\omega, \kappa_c) \) indicates the density of modes with having equal wells. \( \Delta_0 \) has a lower bound \( \Delta_{\min} \) which is the smallest energy splitting below which particles cannot tunnel between two wells within the experimental time scale. Its upper bound is \( E \) where quantum tunnelling contributions dominate. Since \( \Delta_0 \) cannot go to 0, \( 1/(\Delta_0 \sqrt{E^2 - \Delta_0^2}) \) in Eq. (5.4) is thus dominated by \( \Delta_0 \rightarrow E \).

\( P_0 \) is proportional to the density of TLS. Since \( P_0 \) logarithmically increases \(^{†} \) with increasing \( \Delta_0 \), which varies slowly compared to \( 1/(\Delta_0 \sqrt{E^2 - \Delta_0^2}) \) in Eq. (5.4), I set \( \Delta_0 = E \) in \( P_0 \) to estimate it. This choice is based on the above argument that TLS around \( \Delta_0 \sim E \) their density dominates. Correspondingly, following Eq. (5.3) it leads to a typical frequency

\[
\omega_0 = \left( \ln \left( \frac{W}{E} \right) \right)^{1/3} \bar{\omega}.
\]

(5.6)

where \( \omega_0 \) is insensitive to the magnitude of \( E \) since the typical energy splitting \( E \sim k_B T \) at low temperature [127]. Then \( P_0 \) reads

\[
P_0 = \frac{P(\omega_0, \kappa_0) \kappa_0}{18 \hbar} \left[ \ln \left( \frac{W}{E} \right) \right]^{-2}
\]

(5.7)

Now I integrate \( \Delta \) out and obtain

\[
P(E) = \int_{\Delta_{\min}}^{E} P(E, \Delta_0) \, d\Delta_0 \approx P_0 \ln \left( \frac{2E}{\Delta_{\min}} \right)
\]

(5.8)

I set to \( E = 1k_B K \), which would change the magnitude \( P(E) \) only logarithmically. Hence, in my approach, \( \omega_0 \) is regarded as a constant frequency in a given system. \( \Delta_{\min} \approx 10^{-13} k_B K \) when the experimental time scale is chosen to be equal to 100s \(^{§} \).

Notice that the conventional definition of the density of TLS, \( n_0 \), [4] is the number of TLS per volume per energy. Hence

\[
n_0 \equiv \frac{3NP(E)}{V} \approx C_0 P(\omega_0, \kappa_0) \kappa_0,
\]

(5.9)

where \( C_0 \approx \frac{31}{\omega_0 a^3} \left[ \ln \left( \frac{W}{\kappa_0 a^3} \right) \right]^{-2} \) and \( a^3 \equiv V/N \). \( a \) is the interparticle distance. For a given ma-

\(^{†} \) \( P_0 \) would be proportional to \( \left[ \ln \left( \frac{W}{\Delta_0} \right) \right]^{-2/3} \) since \( P(\omega, \kappa_c) \) is proportional to \( \omega^3 \) as discussed in the introduction 0.2 and in chapter 1, and \( \kappa_c \propto \omega \).

\(^{‡} \) If \( E = 10k_B K \), \( P(E) \) only increases by around 70% compared to \( E = k_B K \) where I use \( W = 100K \) and \( P_0 \sim \left[ \ln \left( \frac{W}{E} \right) \right]^{-2/3} \) in this test.

\(^{§} \) The energy \( E \) can be estimated by the formula \( E = \hbar \pi / \tau \) as shown in chapter 3, which indicates the time scale of a state that oscillates between a quantum two level states.

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terial, \( C_0 \) is insensitive to the system preparation since \( a^3 \) slightly changes and the left logarithmic term weekly varies with chemical compositions. Therefore the magnitude of \( n_0 \) is determined by \( P(\omega_0, \kappa_0) \kappa_0 \).

Directly estimating \( P(\omega_0, \kappa_0) \) is hard since it needs exhaustive statistics to fix the normalization factor of \( P(\omega_0, \kappa_0) \). To avoid this problem, I rewrite \( P(\omega_0, \kappa_0) \kappa_0 \) as follows

\[
P(\omega_0, \kappa_0) \kappa_0 = D_L(\omega_0) f_{\omega_0} \quad (5.10)
\]

where

\[
f_{\omega_0} = \frac{P(\omega_0, \kappa_0) \kappa_0}{\int_0^\infty P(\omega_0, \kappa) d\kappa} \quad (5.11)
\]

\( D_L(\omega_0) \) indicates the density of QLMs at \( \omega_0 \), and \( f_{\omega_0} \) is related to the fraction of near equal wells at \( \omega_0 \). Both can be calculated independently from numerical simulations to estimate \( n_0 \).

In a gapless glass, if \( D_L(\omega_0) = A_4 \omega_0^4 \) still holds at \( \omega_0 \), then

\[
n_0 \propto A_4 \quad (5.12)
\]

This explains why \( n_0 \) has a dramatic decrease with decreasing parent temperature [85] since \( A_4 \) dramatically decreases with it as well below \( T_c \) [57, 68]. If there are no double wells (only single wells), despite of magnitude of \( D_L(\omega_0) \), \( n_0 = 0 \) since \( f_{\omega_0} = 0 \). Hence both \( D_L(\omega_0) \) and \( f_{\omega_0} \) influence the magnitude of \( n_0 \).

If \( D_L(\omega) \) is gapped [97, 126] and the gap magnitude \( \omega_c \) is larger than \( \omega_0 \), then \( n_0 \) would decrease significantly. Notice that in section 3.5.2, a necessary condition specifying the experimental time scale for TLS to exist based on the typical frequency \( \omega^*_c \) is given. In my approach here, I have a stringent necessary condition since \( \omega_0 < \omega^*_c \).

### 5.2 Numerical estimation

In this section, I will estimate the values of \( n_0 \) in glasses prepared from different parent temperature \( T_p \) obtained by the SWAP Monte Carlo method.

The typical frequency \( \omega_0 \) depends on \( W \) and \( \tilde{\omega} \) both of which are as a function of \( \chi \).

And \( \chi \equiv c_1 m \omega_D^2 / a^2 \) where dimensionless \( c_1 \) can be estimated numerically. \( \omega_D \) is the Debye frequency. Hence, the typical frequency \( \omega_0 \) reads

\[
\omega_0 = \left( \ln \left( \frac{W}{k_B K} \right) \right)^{1/3} \tilde{\omega} = \omega_D \left[ \left( \frac{c_1}{2} \right) \frac{\hbar \omega_D}{m \omega_D^2 a^2} \ln \left( \frac{\hbar \omega_D}{k_B K} \left( \frac{c_1}{96} \frac{\hbar \omega_D}{m \omega_D^2 a^2} \right)^{1/3} \right) \right]^{1/3} \quad (5.13)
\]

From the above formula, \( \omega_0 \) is approximately proportional to \( c_1^{1/3} \). Suppose that \( c_1 \sim 1, \chi a^4 \sim m \omega_D^2 a^2 \sim 10 eV \) which corresponds to the magnitude of the banding energy, and \( \hbar \omega_D \sim 10 \text{meV} \) (I will have the exact calculations later). Hence, as a rough estimation, \( \omega_0 \sim 0.1 \omega_D \).
5.2. Numerical estimation

For the exact calculations, I explicitly use the parameters of the amorphous silicon to estimate $\omega_0$, where $m \approx 4.8 \times 10^{-26}$ kg, $a \approx 2.4 \times 10^{-10}$ m, and $\omega_D \approx 530 k_B K/h$ [134].

For the most stable gapped glasses prepared by the “breathing particles” method in chapter 3, $\omega_0 \approx 0.15 \omega_D$ which is close to $\omega_c \approx 0.1 \omega_D$. Hence, since $D_L(\omega_0)$ is tiny when $\omega_0$ is close to $\omega_c$, $n_0$ is tiny.

For gapless glasses prepared at different $T_p$, I estimate $D_L(\omega_0)$ and $f_{\omega_0}$ separately. I choose three $T_p$ with the values $T_p = 0.8, 0.55, 0.35$, where the mode-coupling temperature $T_c$ is about 0.8 and the glass temperature $T_g$ about 0.5 [68]. Notice that even in the same material $\omega_D$ at different $T_p$ are slightly different since their bulk elastic moduli increase with decreasing $T_p$. In the numerics, I let $\omega_D = 530k_B K/h$ at $T_p = 0.55$ since it is close to the glass transition temperature.

To capture the local energy landscape better, I use the non-linear modes with coefficients $\omega_1$, $\kappa_1$ and $\chi_1$, which are obtained by the Taylor expansion along the non-linear modes, to estimate $c_1$ and $f_{\omega_0}$. The non-linear modes are obtained by minimising the cost function that starts from the QLMs directions (see the details in ref. [115, 143] called “cubic modes” and in Appendix E.3). $c_1$ is taken from the median of the ratio $\chi_1/(m\omega_D^2/a^2)$. Specifically, $c_1 \approx 2, 3, 9$ correspond to $T_p = 0.8, 0.55, 0.35$, respectively (see appendix E.4 for details). As a result, $\omega_0/\omega_D \approx 0.11, 0.13, 0.19$. $D_L(\omega_0)$, seen in the Table 5.2, is obtained from $D_L(\omega_0) = A_4 \omega_0^4$ since the quartic spectrum of QLMs at $\omega_0$ still holds\(^\dagger\). $A_4$ is extracted from $D_L(\omega)$ in numerics.

$f_{\omega_0}$, from Eq. (5.11), is numerically given by $f_{\omega_0} = (\kappa_e N_1/\delta \kappa_1)/N_t$ around $\omega_0$ where $N_t$ standing for the denominator in Eq. (5.11) is the total number of modes in the range from 0 to $\infty$ for $\kappa_1$, and $N_1$ in the numerator is the number of modes in the range $\kappa_e \pm \delta \kappa/2$ which corresponds to the range around two equal wells. In Fig. 5.1, I show the scatter of $\kappa_1/\sqrt{\chi_1}$ v.s. $\omega_0^2$ at different $T_p$ where I consider the dependence on $\chi_1$. I count $N_1$ between the green curve that corresponds to the two wells with equal depth, and the black curve that corresponds to the spinodal case, in the range $\omega_0^2 \in [0.1, 10]$ (shaded area) instead of around $\omega_0$\(^\circ\). The values of $f_{\omega_0}$ are shown in the Table 5.2. At $T_p = 0.8$, systems are prepared by the normal MD simulations with $N = 8000$.

<table>
<thead>
<tr>
<th>(T_p)</th>
<th>$n_0[f^{-1}m^{-3}]$</th>
<th>$\omega_0/\omega_D$</th>
<th>$C_0[f^{-1}m^{-3}s^{-1}]$</th>
<th>$D_L(\omega_0)[s]$</th>
<th>$f_{\omega_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>$9.8 \times 10^{17}$</td>
<td>0.11</td>
<td>$5.8 \times 10^{22}$</td>
<td>$4.4 \times 10^{-15}$</td>
<td>0.38</td>
</tr>
<tr>
<td>0.55</td>
<td>$3.9 \times 10^{17}$</td>
<td>0.13</td>
<td>$5.1 \times 10^{22}$</td>
<td>$2.8 \times 10^{-15}$</td>
<td>0.27</td>
</tr>
<tr>
<td>0.35</td>
<td>$3.1 \times 10^{15}$</td>
<td>0.19</td>
<td>$3.7 \times 10^{22}$</td>
<td>$2.1 \times 10^{-16}$</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 5.1 – The estimation of the related parameters to get density of TLS $n_0$.

From the above estimation, $C_0$ is insensitive to the system preparation. Both $D_L(\omega_0)$ and

\(^\circ\)Along eigen-modes, $c_1 \approx 0.74, 1.5, 6.0$ at small $\omega$. Since $\omega_0$ is proportional to $c_1^{1/3}$, $\omega_0$ will not be too different compared to the values obtained from non-linear modes I use.

\(^\dagger\)The upper bound of the scaling regime is $20 – 30\%$ of $\omega_D$ [68].

\(^\circ\)I tested that the order of magnitude of $f_{\omega_0}$ will not change if I chose a narrower related range of $\omega_1$. 

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Chapter 5. The connection between the density of TLS and density of QLMs

Figure 5.1 – Scatter of $\kappa_1 / \sqrt{\chi}$ v.s. $\omega_1^2$ for non-linear modes. They correspond to QLMs whose frequencies are below the frequency of the first plane waves. The Green curve indicates the equal double wells and the black curve indicates the spinodal case. In numerics, $\omega_0 \approx 1.6, 2.0, 3.2$ correspond to $T_p = 0.8, 0.55, 0.3$, respectively.

$f_{\omega_0}$ decrease with lowering $T_p$ which leads to the significant decrease in $n_0$ by a factor of 300 times. The estimated $n_0$ agrees well with the experimental measurement of $n_0$ in amorphous silicon [129] which varies between $10^{45} - 10^{48} J^{-1} m^{-3}$. In the most stable glasses at $T_p = 0.3$, $n_0$ will further decrease ††.

5.3 Discussion

The estimated $n_0$ in our approach is $10^2 - 10^3$ times smaller than the estimations of $n_0$ in [85]. I believe that the source of discrepancy is as follows: (a) as the authors stated in [85] they have used the classical thermal activations to probe the DWPs. Most of TLS with small energy splitting that they found would not be found in the experiment, because their tunnelling times go beyond the experimental time scales. (b) The system is different (particle density, pair interaction) which leads to that $A_4$ [57] is quite different from the ref.[68] that I use.

In my model I set $\chi$ to be a constant that is taken from its median value, which is an approximation. However, the estimation is consistent with the experimental results, supporting that: (i) TLS which contribute to the thermal transport correspond to the QLMs with a typical frequency $\omega_0$ that is about $10\% - 20\%$ of $\omega_D$; (ii) the decrease in the density of TLS is not only influenced by the rarefaction of the density of QLMs but also influenced by the decrease of $f_{\omega_0}$. The latter reflects the distribution of local energy shapes, for example, the fraction of double wells will be smaller at a lower temperature with $f_{\omega_0}$ decreasing.

††Sufficient statistics are needed to estimate $f_{\omega_0}$ at lower $T_p$. 

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Conclusion

Summary

In Chapter 1, we provided a theory that establishes the link between QLMs and shear transformations for systems under quasi-static loading. It predicts the density of QLMs, $D_L(\omega) \sim \omega^\alpha$, to display two regimes depending on the density of shear transformations $P(x) \sim x^\theta$ (with $x$ the additional stress needed to trigger a shear transformation). If $\theta > 1/4$, $\alpha = 4$ and a finite fraction of quasi-localised modes form shear transformations, whose amplitudes vanish at low frequencies. If $\theta < 1/4$, $\alpha = 3 + 4\theta$ and all QLMs form shear transformations with a finite amplitude at vanishing frequencies. We confirmed our predictions numerically.

The second regime does not appear in rapidly quenched materials (and is thus presumably absent in foams and granular materials). By contrast it is expected to be very pronounced in real glasses which are much more stable than the ‘slowly quenched’ configurations studied in Chapter 1. This view is supported by recent measurements in simulated glasses prepared by the Swap Monte Carlo method (that are comparable to experimental cooling rates), which indeed show extremely small values for $\theta$ [88]. As a consequence, we predict that in the most ultrastable generated glasses, the exponent $\alpha \approx 3$ close to the yielding transition and $\alpha = 4$ after the yielding. Note that our argument appears to be rather generic, and may apply to other disordered systems with long-range interactions, e.g. in crystals with defects.

In Chapter 2, we introduced a simple computer glass preparation protocol — following ideas put forward in [106] — that enables the generation of ultrastable glasses. By allowing the effective sizes of particles to fluctuate during glass formation, and freezing them thereafter, we are able to generate extremely stable glassy configurations at minimal computational cost. Strikingly, we found that the density of QLMs displays a gap in our most stable computer glasses which is consistent with the lack of plasticity we observed at small stress. We demonstrated that the mechanical stability of our glasses is readily tunable by varying the stiffness associated with the change of effective size, and showed that it is at least comparable to the mechanical stability of glasses created using the Swap Monte Carlo method [88], however with an algorithm that is faster.
In Chapter 3, we have argued that in glasses that present a gap in the density of quasi-localised modes (have no modes with a frequency \( \omega < \omega_c \)), modes beyond the gap \( \omega_c \) act as an excitation reservoir for thermal activation. This effect destroys the gap at any finite temperature and leads to a density of quasi-localised modes \( D_L(\omega) \approx A_4(T) \omega^4 \). At low temperatures, we found that \( A_4 \sim \exp(-E_a(\omega_c)/T) \) where the typical energy scale \( E_a(\omega_c) \) is a rapidly increasing function of \( \omega_c \). A simple scaling prediction gives \( E_a \sim \omega_c^4 \), in good agreement with our observations, except for the smallest gap value that we explore. Finally, we observed that as the gap increases, excitations involve fewer and fewer particles and become more and more string-like. The growing length scale of the excitations as \( \omega_c \to 0 \) is consistent with the previously identified growing length characterising the elastic response of an amorphous solid near a macroscopic elastic instability [136].

Although our observations were made in ultra-stable states obtained by a specific protocol, our arguments on this reservoir effect are expected to be much more general. This reservoir effect suggests a natural way to extend the spectrum of QLMs in infinite dimensions to finite dimensions where the gap of the spectrum is decorated by excitations stemming from the reservoir of modes with \( \omega \geq \omega_c \). Our finding on the string-like rearrangements at largest gap \( \omega_c \) supports that the mean-field proposal that an effective gap grows upon cooling is consistent with the observation in finite dimensions that rearrangements become string-like upon cooling [24, 25].

In Chapter 4, we showed preliminary results on the local excitations in glasses which are prepared by an instantaneous quench from equilibrated configurations obtained by the SWAP Monte Carlo method. We found that in these glasses, (i) rearrangements become string-like when the glass becomes more stable. (ii) \( A_4 \) weakly depends on the quench rate at low temperature \( T_p \). (iii) One local rearrangement can be associated with several QLMs. (iv) We tested the idea that these soft regions are induced by rare fluctuations of key quantities controlling stability, such as coordination and pressure. Our results indicated a clear correlation. Yet, more needs to be done to characterise the geometry of these rare regions. It appears necessary to later estimate how their density depends on the overall stability of the system.

In Chapter 5, I argued that \( n_0 \) is proportional to \( A_4 \) and to the fraction \( f_{\omega_0} \) of double-wells at same characteristic frequency \( \omega_0 \). Based on this argument, I estimated \( n_0 \) in glasses prepared from different parent temperature \( T_p \) obtained by the SWAP Monte Carlo method. I found that \( n_0 \) decreases by a factor of 300 in ultrastable glasses than poorly prepared glasses with both \( A_4 \) and \( f_{\omega_0} \) playing a significant role. More significantly, the estimations of \( n_0 \) are consistent with the order of magnitude of the change in \( n_0 \) found in amorphous silicon [129].
Conclusion

Perspective

In 1995, Anderson [144] wrote that “the deepest and most interesting unsolved problem in solid state theory is probably the nature of glass and the glass transition”. Even nowadays, this problem is still hotly debated. Ignoring the difficulties that the theory meets, we study the problem numerically by using some advanced techniques which paves the way for the construction of the theory. The below two aspects of future steps are discussed.

Tunnelling entities of Two level systems (TLS)

TLS provide a successful phenomenological description for the thermal anomalies at low temperature in glass, but their tunnelling entities are still unclear. Some scientists [9, 145] thought that the tunnelling entities might come from an atom or a group of atoms whose coordination is low, effectively, giving them an extra degree of freedom such as dangling bonds. Others [146, 20] thought that these tunnelling entities come from low mass density regions since in some amorphous solids (for example, amorphous silicon), the density of TLS and the average mass density are correlated. Both two effects above are argued to influence the density of TLS. From the experimental side, it is hard to detect the region where tunnelling occurs. However, based on the recent SWAP Monte Carlo protocol and the efficient “breathing particle” method we are able to prepare ultrastable glasses comparable to those prepared in experiment. We can thus numerically study this question.

To clarify the tunnelling entities, as a first step, we can study the properties of local rearrangements such as their bond force distribution and their local mass density. We can check whether they have difference with immovable particles and study how they change with changing system preparation. As a second step, a first-principle calculation, such as quantum Monte Carlo protocol or path integrals MD protocol, should be developed to calculate the quantum tunnelling effect and energy spectrum for such rearranging particles, which would be possible since only a few number of particles are involved in stable glasses, and there is no “sign problem” in bosonic system.

Stability of glasses

In chapter 2, we found that by allowing the sizes of particles to vary, stable glasses can be prepared leading to a density of quasi-localised modes that is gapped. It would be of interest to investigate how the number of these extra degrees of freedom (by varying the fraction of particles that can breathe) influences the stability of glasses (or the number of quasi-localised modes). Of course, this will affect the dynamics of systems.

We can also look into how the purely repulsive microscopic pair interaction, proportional to \(1/r^n\), where \(n \geq d\), influences the stability of glasses by using the well developed “Ewald summation” technique when running simulations. If \(n\) is small, the long-range interaction is important which makes particles collaborate, and generates quite stable glasses. We would expect that such glasses are brittle and their spectrum of vibrational modes is gapped (ex-
Conclusion

cluding obvious long wave-length Goldstone modes). If \( n \) is big, such as \( n = 10 \), which is a leading order in our simulations presented here, where the short-range interaction dominates, the prepared glasses will be gapless. We would guess that infinite dimensional glasses below \( T_c \), the glasses prepared by the breathing particles method, and the glasses with a long-range interaction (small \( n \)) will be in the same class, all of which are gapped like insulators in the electronic system. Changing \( n \) would be similar to changing the temperature \( T \) in infinite dimensional glasses. This behaviour indicates that the change of rigidity in glasses leading to the change of the degree of freedom of each particle so that the slow dynamics or the glass transition occurs.
A appendix of Introduction

A.1 Random potential argument

This argument [71, 72] is following the spirit of the "soft-potential model" [73, 74, 75] whose potential energy $U(s)$ along a QLM direction $s$ is regarded as a one-dimensional anharmonic oscillator. They consider $U(s)$ to be a smooth random function and expanded it in Taylor series. For simplicity, the potential energy expended to the fourth order of $s$ is

$$U(s) = \frac{1}{4!}\chi' s^4 + \frac{1}{3!}\kappa' s^3 + \frac{1}{2!}\lambda' s^2 + \sigma s,$$  (A.1)

where they set $U(0) = 0$. $\chi'$, $\kappa'$, $\lambda'$ and $\sigma$ is thought to be an random with the joint probability distribution $P(\chi', \kappa', \lambda', \sigma)$ which is assumed to be a smooth function (free of zeros and without singularity). $U(s)$ can also be Taylor expended around its minimum at $s = s_0$ as

$$U(s) = \frac{1}{4!}\chi(s-s_0)^4 + \frac{1}{3!}\kappa(s-s_0)^3 + \frac{1}{2!}\lambda(s-s_0)^2 + \text{constant},$$  (A.2)

where $\lambda = \omega^2$. To know $D_L(\omega)$ we need to know $P(\lambda)$ before. Further to know $P(\lambda)$, we need to know the joint distribution $P(\chi, \kappa, \lambda, s_0)$. The coefficients $(\chi, \kappa, \lambda, s_0)$ in its joint distribution is related to $(\chi', \kappa', \lambda', \sigma)$ by

$$P(\chi, \kappa, \lambda, s_0) = \left| \det \frac{\partial (\chi', \kappa', \lambda', \sigma)}{\partial (\chi, \kappa, \lambda, s_0)} \right| P(\chi', \kappa', \lambda', \sigma) = |\lambda| P(\chi', \kappa', \lambda', \sigma).$$  (A.3)

So the distribution $P(\lambda)$ is

$$P(\lambda) = |\lambda| \int ds_0 d\kappa d\chi P(\chi', \kappa', \lambda', \sigma),$$  (A.4)

where $P(\chi', \kappa', \lambda', \sigma)$ is smooth. At small $\lambda$, if $\chi, \kappa$ are independent and not bounded by $\lambda$, $P(\lambda) \sim \lambda$. If $s_0$ is at the global minimum of the potential which indicates a single well potential, $\kappa$ is bounded by $|\kappa| < \sqrt{8\lambda \chi^2}$. After integrating out $s_0$, $\chi$, and $\kappa$ one will find $P(\lambda) \sim \lambda^{3/2}$. Since $\omega = \sqrt{\lambda}$,

*This Jacobian proportional to $|\lambda|$ was for the first time evaluated in [51].
Appendix A. appendix of Introduction

\[ D_L(\omega) \equiv P(\lambda) \frac{d\lambda}{d\omega} \begin{cases} \omega^3 & \text{at local minimum} \\ \omega^4 & \text{at global minimum} \end{cases} \]  

(A.5)

Namely, according to the above argument, the density of state \( D_L(\omega) \) is proportional to \( \omega^3 \) or \( \omega^4 \) depending on system preparation. If the amorphous solids are well-prepared for example slowly annealed \( D_L(\omega) \sim \omega^4 \). Otherwise \( D_L(\omega) \sim \omega^3 \).

A.2 the derivation of \( \theta \) in the ground state without including interactions

The density of shear transformations \( P(x) \sim x^{2/3} \) if the system is in the ground state, its joint distribution \( P(\omega, \kappa) \sim \omega^3 \), and the interactions between each modes are ignored.

derivation

The potential energy expended to the fourth order of \( s \) is

\[ U(s) = \frac{1}{24} s^4 + \frac{\kappa}{6} s^3 + \frac{1}{2} \omega^2 s^2 - fs \]

where \( f \) is the external force. The force needed \( f_c \) to trigger a shear transformation satisfies \( dU/ds = 0 \) and \( d^2U/ds^2 = 0 \). (\( f_c \) is the maximal slope of the potential without the external force.) Hence,

\[ f_c = \frac{1}{6} s_0^3 + \frac{\kappa}{2} s_0^2 + \omega^2 s_0, \]

where \( s_0 = \kappa - \sqrt{\kappa^2 - 2\omega^2}. \kappa > \sqrt{2}\omega \).

For the ground state, the mode can be triggered by the external force is in the region:

\[ \sqrt{2}\omega < \kappa < \sqrt{\frac{6}{5}}\omega. \]

Now let \( \omega = c\kappa \). Then \( \sqrt{\frac{3}{2}} < c < \sqrt{\frac{1}{2}} \).

\( P(x) \) thus can be expressed by

\[ P(x) = \int_{\sqrt{3/2}}^{\sqrt{172}} dc \int dx P(\kappa, c) \delta(x - f_c(\kappa, c)), \]  

(A.6)

where \( f_c(\kappa, c) = \frac{1}{6} s_0^3 + \frac{\kappa}{2} s_0^2 + \omega^2 s_0 = \kappa^3 \left[ \frac{1}{6} \left( 1 - \sqrt{1 - 2c^2} \right)^3 + \frac{1}{2} \left( 1 - \sqrt{1 - 2c^2} \right)^2 + \left( 1 - \sqrt{1 - 2c^2} \right) \right] \).

We calculate the joint distribution \( P(\kappa, c) \) based on \( P(\omega, \kappa) \sim \omega^3 \),

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A.3. Vibrational instability argument

\[ P(\kappa, c) = P(\omega, \kappa) \left\| \frac{d\omega d\kappa}{d\kappa dc} \right\| = P(\omega, \kappa) \kappa \sim \omega^3 \kappa = c^3 \kappa^4 \]

Now we explicitly integrate out \( \kappa \) in Eq. A.6. Since \( \delta(x - f_c(\kappa, c)) \equiv \frac{\delta(\kappa - \kappa^*)}{f_c(\kappa, c)} \mu c \), where \( \kappa^* = \left( \frac{x}{t(c)} \right)^{1/3} \) and \( f_c(\kappa, c) = \kappa^3 t(c) \),

\[ P(x) = \int_{\sqrt{\frac{1}{3}} \frac{1}{\sqrt{\frac{I_c}{I}}}}^{\sqrt{\frac{1}{3}} \frac{1}{\sqrt{\frac{I_c}{I}}}} dc \int d\kappa P(\kappa, c) \delta(x - f_c(\kappa, c)) \]

\[ \sim \int_{\sqrt{\frac{1}{3}} \frac{1}{\sqrt{\frac{I_c}{I}}}}^{\sqrt{\frac{1}{3}} \frac{1}{\sqrt{\frac{I_c}{I}}}} dc \frac{c^3 (\kappa^*)^2}{t(c)} \]

\[ = x^2/3 \int_{\sqrt{\frac{1}{3}} \frac{1}{\sqrt{\frac{I_c}{I}}}}^{\sqrt{\frac{1}{3}} \frac{1}{\sqrt{\frac{I_c}{I}}}} dc \frac{c^3}{[t(c)]^{5/3}} \]

The integral for \( c \) has no singularity. Hence, \( P(x) \sim x^{2/3} \). .

A.3 Vibrational instability argument

The second is the “vibrational stability argument” [15, 79, 80] which concludes that the \( \omega^4 \) spectrum of QLMs is present from two steps. (1) They consider the low-frequency harmonic oscillators, with the frequency \( \omega' \), interacting with their surrounding high frequency harmonic ones, with the frequency about \( \omega_D \), through the elastic medium. Due to the interaction and by assuming the density of \( \omega' \) smooth, they obtain that the density of the eigen frequency is proportional to \( \omega \) when \( \omega \) approaches zero. (2) Then they use a mean field method that includes the quartic term and the random mechanical noise force term \( F \) as the first method above. Particularly, the distribution of \( F, P(F) \) does not vanish at \( F = 0 \). This leads to an additional factor in \( D_L(\omega) \), which is proportional to \( \omega^3 \) same with the contribution of the joint distribution \( P(\omega, \kappa, \chi) \) above. Finally, they obtain \( D_L(\omega) \sim \omega^4 \).

For the step (1), for simplicity, consider two interacting oscillators having equal mass \( m = 1 \) with their frequencies \( \omega_1 \) and \( \omega_D (\omega_D \gg \omega_1) \) along their reaction coordinates \( s_1 \) and \( s_2 \) respectively. The corresponding potential reads

\[ U(s_1, s_2) = \frac{1}{2} \omega_1^2 s_1^2 + \frac{1}{2} \omega_2^2 s_2^2 + Is_1 s_2. \]

where \( I \) is the interaction strength which is a dipolar form [147]. \( I \) renormalises the low frequency \( \omega_1 \) to lower \( \tilde{\omega}_1 \). For \( I < I_c \equiv \omega_1 \omega_D, \tilde{\omega}_1 \) approaches zero as \( \tilde{\omega}_1 = \omega_1 \sqrt{1 - (I/I_c)^2} \). Hence the reconstructed density of lower frequency modes \( g_1(\omega) \) can be expressed by

\[ g_1(\omega) = \int d\omega_1 g_0(\omega_1) \int_0^{I_c} dIP(I) \delta \left( \omega - \omega_1 \sqrt{1 - (I/I_c)^2} \right). \]
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By assuming $P(I)\text{ smooth and without singularity approaching } I_c$, one will get $g_1(\omega) \propto \omega$ at small $\omega$.

For the step (2), consider an anharmonic oscillator under a random force $f$:

$$U(s) = \frac{1}{4} As^4 + \frac{1}{2} \omega_1^2 s^2 - fs. \quad (A.12)$$

Clearly, the force $f$ shifts the minimum position from $s = 0$ to $s = s_0 \neq 0$ which satisfies $As_0^3 + M\omega_1^2 s_0 - f = 0$. The oscillator at $s_0$ also has a new frequency $\omega_{\text{new}}^2 = \omega_1^2 + 3As_0^2$. Hence one can formally get the renormalised spectrum

$$D_L(\omega) = \int_0^\infty g_1(\omega_1) d\omega_1 \int_{-\infty}^\infty dP(f)\delta(\omega - \omega_{\text{new}}), \quad (A.13)$$

where $g_1(\omega_1) \propto \omega_1$ and $P(f)$ is Lorentzian distributed. For low frequencies $\omega \ll \omega_b$, where $\omega_b$ is the Boson peak, $P(f) \approx P(0)$ because only small random forces $f$ contribute to the second integral in Eq. (A.13). Finally, they got

$$D_L(\omega) \propto \omega^3 \int_0^\omega d\omega_1 \frac{\omega_1}{\sqrt{\omega^2 - \omega_1^2}} \propto \omega^4. \quad (A.14)$$

For $\omega_b \ll \omega \ll \sqrt{I_c}$, the random force contribution to QLMs’ spectrum can be neglected so that $D_L(\omega) \sim \omega$. They verified these scaling behaviours numerically through a lattice model [79]. An elaborate introduction on this “vibrational instability argument” is reported in latest in [148].
B.1 Potential shape dynamics

Here we derive Eq. (1.3) of the chapter 1. Following Eqs. (1.1,1.2), the tilted potential under shear stress in a block \( i \) is

\[
\tilde{u}_i(s, \delta \sigma_i) = \frac{1}{2!} \tilde{\lambda}_i s^2 + \frac{1}{3!} \tilde{\kappa}_i s^3 + \frac{1}{4!} s^4 - s \delta \sigma_i. \tag{B.1}
\]

which can be equivalently expressed as

\[
\tilde{u}_i(s, \delta \sigma_i) = \frac{1}{2!} \tilde{\kappa}_i (s - s_0)^2 + \frac{1}{3!} \tilde{\lambda}_i (s - s_0)^3 + \frac{1}{4!} (s - s_0)^4, \tag{B.2}
\]

where \( s_0 \) is the displacement that corresponds to the new minimum, and \( (\tilde{\lambda}_i, \tilde{\kappa}_i) \) are the new Taylor expansion coefficients around \( s = s_0 \). The relation between \( (\tilde{\lambda}_i, \tilde{\kappa}_i, s_0) \) and \( (\lambda_i, \kappa_i, \delta \sigma_i) \) reads:

\[
\begin{align*}
\delta \kappa_i &\equiv \tilde{\kappa}_i - \kappa_i = s_0 \\
\delta \lambda_i &\equiv \tilde{\lambda}_i - \lambda_i = \tilde{\kappa}_i s_0 - \frac{1}{2} \tilde{\kappa}_i s_0^2 \\
\delta \sigma_i &\equiv \tilde{\lambda}_i s_0 - \frac{1}{2} \tilde{\kappa}_i s_0^2 + \frac{1}{6} \tilde{\kappa}_i s_0^3.
\end{align*} \tag{B.3}
\]

In the limit \( \delta \sigma_i \to 0 \) we obtain

\[
\begin{align*}
\frac{\partial \kappa_i}{\partial \sigma_i} &\equiv \lim_{\delta \sigma_i \to 0} \frac{\delta \kappa_i}{\delta \sigma_i} = \frac{1}{\lambda_i} \\
\frac{\partial \lambda_i}{\partial \sigma_i} &\equiv \lim_{\delta \sigma_i \to 0} \frac{\delta \lambda_i}{\delta \sigma_i} = \frac{\kappa_i}{\lambda_i}.
\end{align*} \tag{B.4}
\]

B.2 Derivation of the parabola \( \kappa^2 - 8 \lambda / 3 = 0 \) after the block fails.

When the block fails, it drops to a new minimum. The potential expands at the new minimum is:

\[
u(s) = \frac{1}{2!} \lambda s^2 + \frac{1}{3!} \kappa s^3 + \frac{1}{4!} s^4. \tag{B.5}
\]
At the inflection point, it satisfies:

\[
\begin{align*}
\frac{du(s)}{ds} &= 0 \\
\frac{d^2 u(s)}{ds^2} &= 0
\end{align*}
\]  

(B.6)

We eliminate \( s \) and obtain the relation: \( \kappa^2 - 8/3 \lambda = 0 \).

### B.3 Derivation of the Jacobian \( |\partial(\Delta \sigma, \Phi)/\partial(\lambda, \kappa)| \)

To calculate the Jacobian \( |\partial(\Delta \sigma, \Phi)/\partial(\lambda, \kappa)| \) we first express \( \sigma \) as a function of \( \lambda \) and \( \kappa \). To this end we substitute \( \lambda = (\kappa^2 - \Phi)/2 \) (Eq. (1.4)) into \( \partial \kappa / \partial \Delta \sigma = 1/\lambda \) (Eq. (1.3)):

\[
\left( \frac{\kappa^2 - \Phi}{2} \right) \frac{\partial \kappa}{\partial \Delta \sigma} = 1,
\]

(B.7)

so that

\[
\frac{1}{6} \frac{\partial (\kappa^3 - 3 \Phi \kappa)}{\partial \Delta \sigma} = 1,
\]

(B.8)

and therefore

\[
\Delta \sigma = \frac{\kappa^3 - 3 \lambda \kappa}{3} + c_0.
\]

(B.9)

where \( c_0 \) is an integration constant. Hence, the Jacobian is:

\[
\begin{vmatrix}
\frac{\partial(\Delta \sigma, \Phi)}{\partial(\lambda, \kappa)}
\end{vmatrix} = \left| \frac{\partial \Delta \sigma}{\partial \lambda} \frac{\partial \Phi}{\partial \kappa} - \frac{\partial \Delta \sigma}{\partial \kappa} \frac{\partial \Phi}{\partial \lambda} \right| = 2 \lambda.
\]

(B.10)

### B.4 Distance to the instability

When \( \Phi > 0 \) we choose the integration constant \( c_0 \) in Eq. (B.9) such that \( x = 0 \) at \( \lambda = 0 \). We find that

\[
x = \frac{\lambda \kappa - \left( \kappa - \text{sign}(\kappa) \sqrt{\kappa^2 - 2 \lambda} \right) (\kappa^2 - 2 \lambda)}{3}.
\]

(B.11)

In the limit \( \lambda \ll \kappa^2 \)

\[
x = \frac{1}{2} \frac{\lambda^2}{\kappa}.
\]

(B.12)

When a block fails, it is reinserted on the parabola \( \kappa^2 - 8/3 \lambda = 0 \) and therefore the distance to instability of the reinserted block is

\[
x^* = \frac{1}{12} \kappa^3 = \frac{2}{3} \Phi^{3/2}.
\]

(B.13)
B.5 System preparation protocol

The glass system that we use is identical to the one by [32]. It consists of a binary mixture of point-masses (‘particles’). All details including all parameters values can be found in its supplementary material.

We consider glasses obtained by two different system preparation protocols. Each glass is represented by an ensemble of one thousand independent realisations. Each realisation is obtained by a temperature quench that starts from a state of thermal equilibrium at a temperature $T = T_0$ that is higher than the glass transition temperature. The two quenching protocols are: (i) an instantaneous quench, referred to as ‘rapid quench’, in which fully overdamped dynamics are used until all the particles’ velocities have converged to zero. Here $T_0 = \frac{\varepsilon}{k_B}$, where $\varepsilon$ is a microscopic energy scale and $k_B$ is Boltzmann’s constant. (ii) a continuous quench, referred to as ‘slow quench’, in which the system is first solidified at a cooling rate of $\dot{T} = 10^{-3} T_0 / t_c$ until the temperature $T = 0.1 T_0$ is reached; overdamped dynamics are then employed to remove the remaining heat. Here, $t_c \equiv \sqrt{m d^2 / \varepsilon}$, $m$ is the mass of each particle and $d$ is the diameter of the ‘small’ particles.

B.6 Measurement of $\gamma_{\text{min}}$

To accurately measure $\gamma_{\text{min}}$ a loading protocol has been developed in which the applied shear $\gamma$ is adaptively refined when an instability. More practically, when an instability is detected the system is rewound to its last known equilibrium state before the instability. The instability using smaller steps for $\delta \gamma$. This protocol is repeated a number of times, such that the value of $\gamma$ at which the instability occurs is characterised with a sufficient accuracy. The instability is detected by monitoring a quantity $Q \equiv \max \left| \delta \vec{r}'_i \right| / (L \delta \gamma)$ where $L$ is the linear system size and $\max \left| \delta \vec{r}'_i \right|$ is the maximal change in the non-affine displacement of a particle, for the given increment in applied affine shear $\delta \gamma$. When the response is elastic, $Q$ is of order one. (Note that the factor $1/L$, used to define a dimensionless $Q$, changes with the system size. We do not expect that this size dependence affects our results because $L \sim N^{\frac{3}{4}}$ changes by a factor of 3.3 between $N = 2000$ and $N = 64000$, which is less than the typical fluctuation of $Q$ in different realisations at fixed $N$.) However, if there is a shear transformation, $Q$ is significantly higher.

To detect the shear transformation we set a threshold $Q_c$ to be much larger than the typical $Q$ in elastic shearing and then monitor the three successive $Q_1, Q_2, Q_3$ that results from the strain history $\gamma_1 < \gamma_2 < \gamma_3$. If $Q_2 < Q_c$ and $Q_1, Q_3 < Q_2$, we go back from $\gamma_3$ to $\gamma_1$ and set the strain increment $\delta \gamma / 10$ (see Fig. B.1). This is repeated until the strain increment is smaller than $10^{-6}$. At this final resolution, we use an additional condition $100 Q_3 < Q_2$ to make sure that $Q$ is discontinuous which implies that the instability is present. In our simulations, the initial strain increment $\delta \gamma = 10^{-4}$ and $Q_c = 100$. In the end, we could ensure the error of $\gamma_{\text{min}}$ to be less than $10^{-5}$.
Figure B.1 – Sketch of the protocol to detect the instability. The cyan curve, the blue curve and the red curve correspond to shear steps $\delta \gamma$, $\delta \gamma/10$, $\delta \gamma/100$, respectively. Dashed curves represent the trial steps. If at some point $Q_2 > \max(Q_1, Q_3, Q_c)$ trial steps are reversed and the strain step is reduced by a factor 10.

### B.7 Finite size effects in $D_L(\omega)$ and relation to $P(\gamma_{\min})$

We now discuss finite size effects that affect the distribution $D_L(\omega)$ at low frequencies. They stem from the fact that the states of the glass are sampled at a given value of the accumulated strain $\gamma$ (see the inset of Fig. 1.2(a) in the main text). As a consequence, there is a finite probability density to sample a state that is arbitrarily close to the next instability and therefore we are more likely to sample a shear transformation. This sampling also prevents us to measure $\theta$ by directly fitting $P(\gamma_{\min})$. Namely, as there will be a uniform probability density of finding a shear transformation close to the instability, $P(\gamma_{\min})$ will be uniform at small values of $\gamma_{\min}$. Note that $\gamma = 0$ is a special point because the system is always sampled directly after an avalanche.

To confirm this explanation we measured exponents $\theta'$ and $\alpha'$ defined by $P(\gamma_{\min}) \sim \gamma_{\min}^{\theta'}$ and $D_L(\omega_{\min}) \sim \omega_{\min}^{\alpha'}$, respectively, where $\omega_{\min}$ is the frequency of the softest quasi-localised mode. Figs. B.2(a,b) compare distributions $D_L(\omega)$ and $D_L(\omega_{\min})$ at three representative strain $\gamma = 0, 0.02, 0.09$. As observed, $\alpha$ and $\alpha'$ are clearly different. The distributions $P(\gamma_{\min})$ are also shown in Figs. B.2(c,d) at the three representative strain. Also the values of $\theta'$ are clearly different from $\theta$, as displayed in main text in Figs. 1.3(a,b).

In Figs. B.3(a,b) we report values of $\theta'$ respectively in rapidly and slowly quenched glasses. In both cases $\theta'$ is practically 0. This confirms our explanation presented above. The corresponding values of $\alpha'$ are shown in Figs. B.3(c,d), for which a reasonable agreement is found with the values predicted by the theory. This confirms our explanation: when a small $\omega_{\min}$ is measured it almost always corresponds to a system sampled by chance close to the instability. Therefore, $D_L(\omega_{\min})$ is dominated by shear transformations even if $D_L(\omega)$ is not. This can be clearly seen by comparing regions where $\alpha = 4$ for all $\gamma$ (both shear transformations and passive modes contribute significantly to $D_L(\omega)$) but $\alpha' < 4$ (shear transformations are dominant).
B.8. Comparison of $\alpha$ obtained using different fitting ranges of $\omega$

Figure B.2 – The left column shows results obtained after a rapid quench of a system of $N = 16000$ particles and the right column after a slow quench for $N = 32000$. (a,b) The comparison between $D_L(\omega)$ and $D_L(\omega_{\text{min}})$ at three representative $\gamma = 0, 0.02, 0.09$ (red, yellow, blue). The black markers on the axes indicate the fitting range of $D_L(\omega_{\text{min}})$. The green markers on the axes indicate the same the fitting range used in the main text (cf. Figs. 1.2(g,h)). (c,d) The distribution of $P(\gamma_{\text{min}})$ at the same three representative $\gamma = 0, 0.02, 0.09$ (red, yellow, blue).

B.8. Comparison of $\alpha$ obtained using different fitting ranges of $\omega$

To test the robustness of the fit of the exponent $\alpha$, we measure it using different lower bounds of the range over which $D_L(\omega)$ is fit. Note that at this point plane waves have been filtered out by the protocol described in the main text. This has set the upper bound of the fitting range to be there where the power-law scaling is clearly interrupted by the plane waves. In Fig. B.4(a,b) we show that there is a range of lower bounds for which the measured values of $\alpha$ are robust in rapidly and slowly quenched glasses, respectively.

B.9. $\theta$ and $\alpha$ in steady state in rapidly quenched systems

In the steady state, $\theta$ and $\alpha$ should no longer depend on the system preparation. In Figs. B.5(a,b) we show $\theta$ and $\alpha$ at large strains for the system prepared by a rapid quench. Clearly, $\theta$ converges to a constant larger than $1/4$ and $\alpha \approx 4$. 
Appendix B. Appendix of chapter 1

Figure B.3 – The left column shows results obtained after a rapid quench for $N = 16000$ using 1000 realisations and the right column results obtained after a slow quench for $N = 32000$ using 5000 realisations. (a,b) $\theta'$ is obtained by fitting $P(\gamma_{\text{min}})$ at different $\gamma$. (c,d) Measured values of $\alpha'$ (red line) are in good agreement with the theoretical prediction $\alpha' = 4\theta' + 3$ (blue line).

Figure B.4 – $\alpha$ measured at different lower bounds of fitting ranges after (a) a rapid quench and (b) a slow quench. The results that are reported in the main text (Figs. 1.3(c,d)) correspond to the red lines.

Figure B.5 – (a) $\theta$ obtained from finite size scaling analysis in steady state. (b) The density of states of quasi-localised vibrational modes $D_L(\omega)$ at low frequencies $\omega$ for $N = 16000$ after modes with a participation ratio above the threshold $e_c$ have been removed. The green markers on the axes indicate the same fitting range that is used in the main text (cf. Fig. 1.2(g)).
C appendix of chapter 2

C.1 Observables

C.1.1 Vibrational modes

Vibrational modes were calculated by a numerical partial diagonalization of the dynamical matrix \( \mathcal{M} \equiv \frac{\partial^2 U}{\partial x \partial x} \), where \( U \) is the potential energy as given by Eq. (2.4), and \( x \) denotes the vector of \( 3N \) particles’ Cartesian coordinates. We employed the ARPACK package [149].

C.1.2 Athermal elastic moduli

The shear stress is given by

\[
\sigma = \frac{1}{V} \frac{\partial U}{\partial \gamma},
\]

where \( \gamma \) denotes a simple shear strain. Athermal elastic moduli were calculated following the formulation of Lutsko [95]. The shear modulus \( G \) is given by

\[
G = \frac{\frac{\partial^2 U}{\partial \gamma^2} - \frac{\partial^2 U}{\partial \gamma \partial x} \cdot \mathcal{M}^{-1} \cdot \frac{\partial^2 U}{\partial x \partial \gamma}}{V},
\]

and the bulk modulus \( K \) by

\[
K = \frac{\frac{\partial^2 U}{\partial \eta^2} - \frac{\partial^2 U}{\partial \eta \partial x} \cdot \mathcal{M}^{-1} \cdot \frac{\partial^2 U}{\partial x \partial \eta}}{V - d^2} + p.
\]

Here \( p \equiv -\frac{1}{V^2} \frac{\partial U}{\partial \eta} \) is the hydrostatic pressure, \( V \) is the system’s volume, and \( \gamma, \eta \) are simple shear and expansive strains, respectively, that parametrize the 3D strain tensor as

\[
\epsilon = \frac{1}{2} \begin{pmatrix}
2\eta + \eta^2 & \gamma + \gamma \eta & 0 \\
\gamma + \gamma \eta & 2\eta + \eta^2 + \gamma^2 & 0 \\
0 & 0 & 2\eta + \eta^2
\end{pmatrix}.
\]
C.2 Athermal quasistatic deformation

In addition to various static structural analyses of our glassy samples, we have also carried out conventional athermal quasistatic deformation simulations to test the stability of our glassy samples by studying their transient elasto-plastic response. We imposed increments of simple shear deformation by applying the following transformation of coordinates

\[
\begin{align*}
    x_i &\rightarrow x_i + \delta \gamma y_i, \\
    y_i &\rightarrow y_i, \\
    z_i &\rightarrow z_i,
\end{align*}
\]

using strain steps of \(\delta \gamma = 10^{-3}\). Each such transformation was followed by updating the images of the Lees-Edwards periodic boundary conditions [95], and then minimizing the potential energy \(U\) using a conventional conjugate gradient algorithm.

![Figure C.1](image)

**Figure C.1** – (a) Stress-strain curves for computer glasses made with \(k_\lambda = 10^2\), in which the two possible shear banding geometries occur, as shown in panels (b) and (c). The color code of particles, which represents the magnitude of nonaffine displacements, is the same as in Fig. 2.7.

In our deformation simulations, shear banding events can occur in two different geometries, as demonstrated in Fig. C.1: they can be parallel to the \(x\)-\(z\) plane, as shown in panel (c), or parallel to the \(y\)-\(z\) plane, as shown in panel (b). In Fig. C.1a we show that the resulting strain-strain curves in these two cases are different; in the former, the stress is stationary after the shear band (at least up to the maximal imposed deformation of 20%), whereas in the latter the stress increases after the event. In Fig. 2.7 we only show data pertaining to events with the
C.2. Athermal quasistatic deformation

geometry as displayed in panel (c).
D appendix of chapter 3

D.1 Nomenclature

Symbols

\( n \) number of independent realisations in the ensemble
\( N \) number of particles in one realisation, labelled with indices \( i = 1, \ldots, N \)
\( \mathbf{r}_i \) particle position; vector in three-dimensional Cartesian coordinates
\( \delta \mathbf{r}_i \) particle displacement vector
\( R_i \) particle radius
\( k_B \) Boltzmann's constant
\( m \) particle mass (the same for all particles)
\( L \) linear size of the box which has the same length in three directions
\( V \) volume of the box \( \equiv L^3 \) (since pressure is fixed, \( L \) fluctuates from realisation to realisation)
\( \rho \) number density \( \equiv N/\langle V \rangle \)
\( V_p \) volume occupied by particles \( \equiv \sum_{i=1}^{N} \frac{4}{3} \pi R_i^3 \)
\( \phi \) packing fraction \( \equiv V_p/V \)
\( K \) 'stiffness' with which the particle radius is drawn to its initial value during preparation
\( \omega \) vibrational frequency
\( T_p \) temperature during preparation using 'breathing' dynamics
\( t_p \) duration at which the temperature is fixed to \( T_p \) during preparation
\( T_a \) temperature during thermal activation using normal molecular dynamics (MD)
\( t_a \) duration at which the temperature is fixed to \( T_a \) during thermal activation
\( T_c \) mode-coupling temperature
\( \langle n_e \rangle \) average number of excitations per realisation
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Units

- Lengths ($\vec{r}$, $R_i$ and $L$) are shown in the unit of $d_0$ (or the most frequent diameter of small particles $d_0^*$, if so indicated): the diameter of an initially small particle.

- Energies ($E_a$) are expressed in the unit of $\varepsilon$: the prefactor of the pair interaction potential.

- Temperature ($T_p$, $T_a$, and $T_c$) is in the unit of $\varepsilon/k_B$ where $k_B$ is Boltzmann's constant.

- Time ($t_p$, $t_a$, and $\omega^{-1}$) is shown in the unit of $t_0$ where $t_0 \equiv \sqrt{md_0^2/\varepsilon}$.

Parameters & Key quantities

<table>
<thead>
<tr>
<th>$K$</th>
<th>$1e2$</th>
<th>$1e3$</th>
<th>$3e3$</th>
<th>$1e4$</th>
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<td>1.19</td>
<td>0.85</td>
<td>0.65</td>
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<td>$3e3$</td>
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<td>$8e3$</td>
<td>$8e3$</td>
<td>$8e3$</td>
</tr>
<tr>
<td>$\phi$</td>
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<td>0.74</td>
<td>0.77</td>
<td>0.79</td>
</tr>
<tr>
<td>$\langle V \rangle$</td>
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<td>7303.9 ± 0.7</td>
<td>8607.2 ± 0.9</td>
<td>9356 ± 1</td>
</tr>
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<td>0.86</td>
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<td>0.44</td>
<td>0.49</td>
</tr>
<tr>
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<td>$1e4$</td>
<td>$1e4$</td>
<td>$1e4$</td>
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<tr>
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<td>0.525</td>
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<td>[0.07, 0.10, 0.20, 0.30, 0.39, 0.50, 0.60, 0.80]</td>
<td>[0.03, 0.05, 0.1]</td>
<td>[0.03, 0.05, 0.10, 0.20, 0.30, 0.49, 0.60, 0.80]</td>
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<td>$t_a$</td>
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<td>[1e2, 5e2, 1e4]</td>
<td>[5e2]</td>
<td>[1e2, 5e2, 2e3]</td>
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<td>$E_a$</td>
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<td>0.042 ± 0.016</td>
<td>0.03 ± 0.007</td>
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<td>-</td>
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<td>0.89</td>
<td>1.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Note that the notation $2e3 \equiv 2 \times 10^3$; that $\langle V \rangle$ is the ensemble average volume (and the uncertainty its standard deviation); and that $\langle n_e \rangle$ has been obtained with $t_a = 500$ at the lowest $T_a$ we probed for each $K$. $T_c$ is obtained from the relation: relaxation time $\sim (T - T_c)^{-\nu}$ [3], where $\nu$ is also a fit parameter.
Detecting a rearrangement

To detect if reheating with a temperature $T_a$ for a duration of $t_a$ has led to a rearrangement we consider the ratio of the norm and the participation ratio of the displacement field:

$$\mathcal{I} \equiv \frac{||\delta \vec{r}_i||}{P_r(\delta \vec{r}_i)}$$  \hspace{1cm} (D.1)

where $||\delta \vec{r}_i||$ is the Euclidean norm of the particle displacement field, $\delta \vec{r}_i$, between the quenched states before and after reheating, and its participation ratio

$$P_r(\delta \vec{r}_i) = \frac{(\sum_i ||\delta \vec{r}_i||^2)^2}{N\sum_i ||\delta \vec{r}_i||^4}$$  \hspace{1cm} (D.2)

If a rearrangement results from reheating, the norm of the displacement field is finite (typically $10^{-3} - 10^{-2}$) and participation ratio in the order of $10^{-3} - 10^{-2}$. In contrast, if there was no rearrangement, the norm of the displacement field is of the order of the numerical precision ($10^{-6}$) and the participation ratio is of order one. We distinguish the two cases using a threshold. We define that a rearrangement has taken place if $\mathcal{I} > 10^{-3}$. Note that the distributions of $\mathcal{I}$ corresponding to the two cases are clearly separated.

D.2 Molecular dynamics

Sample preparation: ‘breathing’ dynamics

We study a three-dimensional periodic particle system of $N = 8000$ particles, that is characterised by the grand potential

$$\mathcal{U} = \sum_{i<j} \varphi(r_{ij}, R_i, R_j) + \sum_i \mu\left( R_i, R_i^{(0)} \right)$$  \hspace{1cm} (D.3)

where $\varphi$ is a purely repulsive inverse power-law potential, defined

$$\varphi(r_{ij}, R_i, R_j) = \begin{cases} 
\varepsilon \left[ \left( \frac{R_{ij}}{r_{ij}} \right)^{10} + \sum_{p=0}^{3} c_{2p} \left( \frac{r_{ij}}{R_{ij}} \right)^{2p} \right], & \frac{r_{ij}}{R_{ij}} \leq r_c \\
0, & \frac{r_{ij}}{R_{ij}} > r_c
\end{cases}$$ \hspace{1cm} (D.4)

with $r_c$ is the cutoff distance, $R_{ij} = R_i + R_j$ (two times the average particle radius), and $r_{ij} = ||\vec{r}_{ij}|| = ||\vec{r}_i - \vec{r}_j||$ (the Euclidean norm of the distance vector separating particles $i$ and $j$). $c_{2p}$ is a constant that makes $\varphi$ continuous up to the third derivative at $r_c$. Furthermore,

$$\mu\left( R_i, R_i^{(0)} \right) = \frac{K}{2} \left( 1 - \frac{R_i^{(0)}}{R_i} \right)^2 \left( R_i^{(0)} \right)^2$$ \hspace{1cm} (D.5)
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is a chemical potential that allows a particle to change its size from its initial value \( R_i^{(0)} \) at an energetic cost that scales with a modulus \( K \). For \( K = \infty \) it is impossible for a particle to change its radius, while it becomes easier as \( K \to 0 \). The initial particle radii are bi-disperse, in a 50:50 mixture. In particular, one, randomly selected, half of the particles has \( R_i^{(0)} = 0.5d_0 \) and the other half has \( R_i^{(0)} = 0.7d_0 \) (where \( d_0 \) sets the unit of length of our system).

Sample preparation proceeds by instantaneously heating the initial random configuration to a temperature \( T_p \) and keeping it at this temperature for a certain time \( t_p \) under the constraint of a fixed pressure \( p = 20.0 \) (in units of \( \varepsilon / d_0^3 \)). We then instantaneously quench the system to zero temperature by minimising the grand potential. See algorithmic details below.

Activation by temperature: normal dynamics

We proceed by fixing the particle size, which corresponds to a potential energy

\[
U = \sum_{i<j} \varphi(r_{ij}, R_i, R_j) \tag{D.6}
\]

(see eq. (D.4) for the definition of \( \varphi \)). We then gently heat the system configuration to a certain “activation temperature” \( T_a \) (at a heating rate \( T_a/(10t_0) \)), and keep the sample at \( T_a \) for a total duration \( t_a \). Thereafter we instantaneously quench the sample to zero temperature. Algorithmic details are listed below.

Molecular dynamics algorithm

We run molecular dynamics, whereby the particle dynamics are given by Newton’s equation of motion with the gradient of the potential energy on a particle as driving force. Time is discretised in steps of \( \Delta t \) using the standard velocity Verlet algorithm. The temperature and pressure are controlled using a Berendsen thermostat [111], where the temperature is defined as the total kinetic energy \( \sum_i m(\dot{\mathbf{r}}_i)^2/2 \) (where \( \dot{\mathbf{\cdot}} \) refers to the time derivative). Note that during preparation the kinetic energy is \( \sum_i (m(\dot{\mathbf{r}}_i)^2 + \dot{R}_i^2)/2 \). We use the ‘FIRE’ algorithm [110] to quench the systems.

For completeness we report that \( r_c = 1.48d_0 \), \( \varepsilon = 1 \), \( m = 1 \), \( d_0 = 1 \), and \( \Delta t = 0.005 \). Furthermore \( c_0 = -1.110637662511798 \), \( c_2 = 1.267615237297065 \), \( c_4 = -0.4960406072849212 \), \( c_6 = 0.0660511826415732 \); see Supplemental Material of [76].

D.3 Sample preparation

We choose \( T_p \) and \( t_p \) to empirically generate a configuration in the lowest possible energetic state in terms of the mean interaction energy \( \langle u \rangle = \langle U \rangle / N \) (averaged on an ensemble of \( n = 10 \) samples). In particular, we set \( t_p = 10^4 \) (the highest value we can practically reach, with each sample taking eight CPU hours to prepare). We manually optimise \( T_p \) as reported in fig. D.1. Note that we verify that the \( T_p \) at which we find the optimum, is robust in terms of preparation duration \( t_p \), by comparing our results to those for \( t_p = 500 \) (dashed line in fig. D.1).
Furthermore, the reader is reminded that although the particle size distribution depends on temperature while still at $T_p$, the final particle size distribution at zero temperature is independent of $T_p$. Note that our ‘breathing’ dynamics (at small $K$) are quite efficient to prepare samples in a low potential energy state. We verify this by preparing an ensemble (again $n = 10$, but with $N = 2000$ particles) with normal dynamics and a slow quench rate. We plot the potential energy $\langle u \rangle$ at different temperatures in fig. D.2. In all cases $\langle u \rangle$ at $T = 0$ is higher than that for the sample prepared using ‘breathing’ dynamics, which was prepared at a fraction of the computational costs (sample preparation is a factor of 2000 faster using ‘breathing’ dynamics).

![Figure D.1 – Mean interaction potential energy $\langle u \rangle$ after sample preparation with ‘breathing’ dynamics for varying parent temperature $T_p$ and two different waiting times $t_p$. The different panels correspond to different $K$ as indicated. The selected temperature $T_p$ for which the potential energy is lowest for the largest practically reachable $t_p = 10^4$ is indicated using vertical lines (see appendix D.1 for numeric values).]

**D.4 Measurement of quasi-localised modes**

**Spectrum of the Hessian**

We extract the Hessian (or stiffness matrix) – the second derivative of interaction energy – as follows

$$\mathcal{H}_{ij} \equiv \frac{\partial^2 U}{\partial \vec{r}_i \partial \vec{r}_j} = -\frac{d^2 \varphi(r_{ij})}{dr_{ij}^2} \frac{\hat{r}_{ij}}{r_{ij}^2} \left( \mathcal{F} - \frac{\hat{r}_{ij} \hat{r}_{ij}}{r_{ij}^2} \right)$$

for $i \neq j$. The diagonal

$$\mathcal{H}_{ii} = -\sum_{i \neq j} \mathcal{H}_{ij}$$

due to translation symmetry. Note that $\mathcal{H}_{ij}$ is a second-order tensor, and that $\mathcal{F} = \delta_{\alpha \beta} \hat{e}_\alpha \hat{e}_\beta$ is a second order unit tensor. We then diagonalise the Hessian, leading to $N$ eigenvalues $\lambda$ and corresponding eigenmodes $\vec{\Phi}_i$. Because all particles have a mass $m = 1$ the corresponding $N$...
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Figure D.2 – Mean interaction potential energy as obtained by sample preparation using ‘breathing’ dynamics (at $T = 0$ for $K = 10^2$, $t_p = 10^4$, and $T_p = 0.2$, in black) and using normal dynamics at different cooling rates (cooling from $T = 0.4$) as indicated in the legend. Note that in both cases the ensemble comprises $n = 10$ samples, but that normal dynamics are run using smaller than usual samples comprising $N = 2000$ particles ($N = 8000$ is used throughout). We verify the representativeness of these smaller samples using $N = 8000$ for $\dot{T} = 10^{-3}$, shown using a dashed red line (that indeed coincides with the solid red line for $N = 2000$). The required CPU time to run the entire simulation with $N = 2000$ particles is indicated. Note that for our ‘breathing’ dynamics the time has been divided by four to correct for the difference in system size.

eigenfrequencies are

$$\omega \equiv \sqrt{\lambda} \quad (D.9)$$

We finally represent the spectrum of the Hessian as

$$D(\omega) = \frac{1}{3N - 3} \sum_{k=1}^{3N-3} \delta(\omega - \omega_k) \quad (D.10)$$

**Density of quasi-localised modes**

The density of quasi-localised modes, $D_L(\omega)$, follows from the spectrum of the Hessian in eq. (D.10) by filtering plane waves that have a frequency $\omega_e < \omega_c$ (where $\omega_c$ is defined below). We identify these plane waves by their signature in participation ratio

$$P_r(\Phi_i) = \frac{\left(\sum_i ||\Phi_i||^2\right)^2}{N \sum_i ||\Phi_i||^4} \quad (D.11)$$

Plane waves thereby have $P_r \approx 2/3$, while quasi-localised modes have $P_r \ll 1$.

In practice, most of our samples have no plane waves below $\omega_c$, rendering filtering obsolete. In fact, we only apply filtering after sample preparation for $K = \{10^2, 10^3\}$. Since we empirically observe the plane waves to be well separated from the quasi-localised modes in terms of frequency, we remove them by removing the first $3 + 12 + 24$ eigenmodes of each realisation for $K = 10^3$ and $3 + 12 + 24$ eigenmodes of each realisation for $K = 10^2$, corresponding the 3 translational
D.4. Measurement of quasi-localised modes

modes and the first (two) bands of plane waves*. Note that $D_L(\omega)$ is not renormalised after filtering of plane waves.

We emphasise that in all other measurements $D_L(\omega) = D(\omega)$ at low frequency.

**Protocol to measure $\omega_c$**

We measure the gap frequency $\omega_c$ – the frequency of the first quasi-localised mode. To measure $\omega_c$, we assert that the density of soft quasi-localised modes follows

$$D_L(\omega) \sim (\omega - \omega_c)^\zeta$$

(D.12)

at low frequency $\omega$. We then move $\omega_c$ until the power law is most obvious at low $\omega$, as shown in fig. D.3. We then visually extract the power $\zeta$ and check that it and the extracted $\omega_c$ are consistent with extreme-value statistics. In particular, we expect

$$\omega_{\text{min}}' - \omega_c \sim (n')^{-1/(1+\zeta)}$$

(D.13)

where $\omega_{\text{min}}'$ is the frequency of the softest quasi-localised mode in an ensemble of $n'$ realisations chosen as a random subset of our ensemble of $n$ realisations. We consider $\bar{\omega}_{\text{min}}'$ the average of lowest three realisations (out of $n'$ realisations). Indeed, our extracted $\omega_c$ is consistent with this scaling, as shown in the insets of fig. D.3. In addition, we check that $\omega_c$ is robust to a change of system size (shown in blue in fig. D.3).

![Figure D.3 – Fit of $\omega_c$ by asserting the power law scaling in eq. (D.12) and check by extreme value statistics as in eq. (D.13) (insets), for all considered $K$.](image)

*For $K = 10^3$, $\omega_e = 1.30 \pm 0.02$, and for $K = 10^4$, $\omega_e = \{1.26 \pm 0.03, 1.73 \pm 0.05\}$ (where the uncertainty refers to the standard deviation).
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Protocol to fit $A_4$

$A_4$ is extracted from $D_L(\omega)$ by fitting

\[ D_L(\omega) = A_4 \omega^4 \]  

(i.e. eq. (3.1)) for frequencies below the first plane wave (for $K = 10^2$) and for frequencies below $\omega_c$ (for $K = 10^3$, $3 \times 10^3$, and $10^4$). Note that consequently $D_L(\omega) = D(\omega)$ in the relevant frequency range for all these measurements. The mean and the error of $A_4$ follow as the mean and standard deviation of $[\ln D(\omega_i) - 4 \ln \omega_i]$ where $\omega_i$ corresponds to the position of the bins of $D(\omega)$.

We verify that the value of $A_4$ that we fit is robust to a mild decrease of system size (using $n = 2000$ realisations of $N = 4000$ particles, compared to an ensemble of $n = 4000$ realisations of $N = 8000$ particles). We find that both the density of soft quasi-localised modes and the extracted $A_4$ are robust to the change of system size, as reported in fig. D.4.

![Figure D.4](image_url)

Figure D.4 – (a) $D(\omega)$ for different system sizes $N$ and different activation temperatures $T_a$ (as indicated in the legend). (b) $A_4$ fitted on (a) as a function of $1/T_a$. Both plots are for $K = 10^2$ and $t_a = 500$.

Protocol to fit $E_a$ and $\gamma$

Our protocol to fit $E_a$ and extract $\gamma$ consists of two steps. 1) We first collapse the curves of $A_4(T_a)$ for different $t_a$. Thereto we shift the horizontal axis of e.g. fig. 3.3(b) in accordance with assuming a functional dependence

\[ A_4 = A_4 \left( t_a \gamma e^{-E_a/T_a} \right) \]  

until the curves for different $t_a$ collapse to a single curve (e.g. fig. 3.3(c)), by optimising the ratio $\gamma/E_a$. 2) On the master curve we next fit $E_a$ of low $T_a$. Since we know the ratio $\gamma/E_a$, the fitted value of $E_a$ gives us direct access to $E_a$. Specifically, we fit $\ln(A_4)$ vs $1/T_a - \gamma/E_a \ln t_a$ using linear regression to get $E_a$ and its error at low $T_a$ (the lowest 5 data points in fig. 3.3(c)).
D.5. The Jacobian of the transformation from $(\lambda_1, \kappa_1, \chi_1)$ to $(\lambda_2, \kappa_2, \chi_2)$

Results for different $K$

In fig. D.5 we show the collapse of different waiting times $t_a$ and the fit of $E_a$ at low $T_a$ for all ensembles that are not shown in the main text (notably fig. 3.3). Note that for $K = 3 \times 10^3$ we extract $E_a$ by directly fitting for low $T_a$ for a single $t_a$.

![Figure D.5](image)

Figure D.5 – Fitting of $E_a$ and $\gamma$ for all $K$ not shown in the main text. The fitted values are reported in appendix D.1.

Robustness of $E_a$

In fig. D.6 we verify that the consistency with $E_a \sim \omega^4_c$ is robust to a different measure of the softest quasi-localised mode after sample preparation. In particular, we compare with $\omega_{\text{min}}$.

![Figure D.6](image)

Figure D.6 – $E_a$ as a function of $\omega_c$ (open markers) or as a function of $\omega_{\text{min}}$ (solid markers).

D.5 The Jacobian of the transformation from $(\lambda_1, \kappa_1, \chi_1)$ to $(\lambda_2, \kappa_2, \chi_2)$

![Figure D.7](image)

Figure D.7 – Double-well potential.

The potential around the state 1 is given by:

$$E(s) = \frac{1}{2!} \lambda_1 s^2 + \frac{1}{3!} \kappa_1 s^3 + \frac{1}{4!} \chi_1 s^4 + \text{constant}$$  \hspace{1cm} (D.16)
with the joint distribution \( P(\lambda_1, \kappa_1, \chi_1) \). For the new minimum, state 2, the potential reads:

\[
E(s) = \frac{1}{2!} \lambda_2 (s + s_0)^2 + \frac{1}{3!} \kappa_2 (s + s_0)^3 + \frac{1}{4!} \chi_2 (s + s_0)^4 + \text{constant (D.17)}
\]

where \( s_0 \) is the shift along \( s \), see fig. D.7; and the corresponding joint distribution is \( P(\lambda_2, \kappa_2, \chi_2) \).

The relation between two sets of coefficients \( \lambda_1, \kappa_1, \chi_1 \) and \( \lambda_2, \kappa_2, \chi_2 \) is

\[
\begin{align*}
\chi_1 &= \chi_2 \\
\kappa_1 &= \kappa_2 + \chi_2 s_0 \\
\lambda_1 &= \lambda_2 + \kappa_2 s_0 + \frac{1}{2} \chi_2 s_0^2
\end{align*}
\]

(D.18)

where \( s_0 \) as a function of \( \lambda_2, \kappa_2, \chi_2 \) follows from the fact that the linear term vanishes in eqs. (D.16) and (D.17). In particular,

\[
6\lambda_2 + 3\kappa_2 s_0 + \chi_2 s_0^2 = 0 \quad \text{(D.19)}
\]

The joint distribution \( P(\lambda_2, \kappa_2, \chi_2) \) is given by

\[
P(\lambda_2, \kappa_2, \chi_2) = \left| \frac{\partial^3}{\partial \lambda_1 \partial \kappa_1 \partial \chi_1} \right| P(\lambda_1, \kappa_1, \chi_1)
\]

where

\[
\left| \frac{\partial^3}{\partial \lambda_1 \partial \kappa_2 \partial \chi_2} \right| \equiv \left| \frac{\partial^3}{\partial \lambda_2 \partial \kappa_1 \partial \chi_1} \right| = \left| 1 + \kappa_2 \frac{\partial s_0}{\partial \lambda_2} + \chi_2 \frac{\partial s_0}{\partial \kappa_2} \right|
\]

(D.20)

From eq. (D.19) we find that

\[
\begin{align*}
\frac{\partial s_0}{\partial \lambda_2} &= -\frac{6}{3\kappa_2 + 2\chi_2 s_0} \\
\frac{\partial s_0}{\partial \kappa_2} &= -\frac{3s_0}{3\kappa_2 + 2\chi_2 s_0}
\end{align*}
\]

(D.21)

And thus:

\[
\left| \frac{\partial^3}{\partial \lambda_1 \partial \kappa_2 \partial \chi_2} \right| = \left| -3\kappa_2 - \chi_2 s_0 \right| = \left| \frac{6\lambda_2}{3\kappa_2 s_0 + 2\chi_2 s_0^2} \right|
\]

(D.22)

If the excited state of the double-well potential is close to the spinodal case, \( \lambda_2 \) is small (as it is in fig. D.7). In particular, when \( \lambda_2 \approx 0 \), it follows that \( s_0 \approx -3\kappa_2 / \chi_2 \). Inserting this in eq. (D.24) gives:

\[
\left| \frac{\partial^3}{\partial \lambda_1 \partial \kappa_2 \partial \chi_2} \right| \approx \left| \frac{2\lambda_2 \chi_2}{3\kappa_2^2} \right| \approx \frac{\lambda_2}{\lambda_1} \approx \lambda_2
\]

(D.23)

where \( \lambda_1 \) is a large value with the lower bound \( \omega_2^2 \). We have thus found that the joint distribu-
D.6. Estimation of $\chi_1$

$$P(\lambda_2, \kappa_2, \chi_2) \sim \lambda_2 P(\lambda_1, \kappa_1, \chi_1) \quad (D.26)$$

Hence, the marginal distribution $P(\lambda_2) \sim \lambda_2$ (after integrating out $\kappa_2$ and $\chi_2$) and therefore

$$D(\omega_2) = P(\lambda_2) \frac{d\lambda_2}{d\omega_2} \sim \omega_2^3. \quad (D.27)$$

**Gap in energy barrier distribution**

For a given $\lambda_1$ we define $c(\kappa_1, \chi_1) = \lambda_1 \chi_1 / \kappa_1^2$, which smoothly varies in a narrow range from $1/3$ (for a symmetric double-well) to $3/8$ (for a spinodal). Then we can express the energy barrier as

$$\Delta E = \lambda_1^2 \frac{(3 - \sqrt{9-24c})^2 (3 + 12c + \sqrt{9-24c})}{192 \chi_1 c^2} \quad (D.28)$$

The function $c$ is slowly varying and not singular so that

$$\Delta E \sim \lambda_1^2 \sim \omega_\epsilon^4 \quad (D.29)$$

Similarly, the energy difference

$$E_{12} = \lambda_1^2 \frac{(3 + \sqrt{9-24c})^2 (3 + 12c - \sqrt{9-24c})}{192 \chi_1 c^2} \sim \lambda_1^2 \sim \omega_\epsilon^4 \quad (D.30)$$

(except in the case of a symmetric double-well).

**D.6 Estimation of $\chi_1$**

Numerically, the coefficient $\chi_1$ (from eq. (3.2)) along the direction of the displacement field $\vec{s}$ from the initial minimum to the new minimum whose frequency is smaller than $\omega_\epsilon$ (the frequency of first tranverse plane waves), can be expressed by the pair interaction $\varphi(\vec{r})$ at mechanical equilibrium, as follows:

$$\chi_1 = \sum_{a,\beta,\eta,v=1}^{3} \sum_{n,m,k,l=1}^{N} \frac{\delta U}{\partial r^a_i \partial r^\eta_j \partial r^\beta_k \partial r^v_l} r^a_i s^\beta_j s^\eta_m s^v_n \quad (D.31)$$

$$= \sum_{i<j} \left\{ \left( \frac{1}{r^4_{ij}} \frac{d^4 \varphi}{dr^4} - \frac{6}{r^5_{ij}} \frac{d^3 \varphi}{dr^3} + \frac{15}{r^6_{ij}} \frac{d^2 \varphi}{dr^2} - \frac{15}{r^7_{ij}} \varphi' \right) (\vec{r}_{ij} \cdot \vec{s}_{ij})^4 \right\} + \left( \frac{1}{r^3_{ij}} \frac{d^3 \varphi}{dr^3} - \frac{3}{r^4_{ij}} \frac{d^2 \varphi}{dr^2} + \frac{3}{r^5_{ij}} \varphi' \right) 6 (\vec{r}_{ij} \cdot \vec{s}_{ij})^2 (\vec{s}_{ij} \cdot \vec{s}_{ij}) + \left( \frac{1}{r^2_{ij}} \frac{d^2 \varphi}{dr^2} - \frac{1}{r^3_{ij}} \varphi' \right) 3 (\vec{s}_{ij} \cdot \vec{s}_{ij})^2 \right\} \quad (D.32)$$

where $\vec{r}_i$ are the particles’ equilibrium positions, $\vec{s}$ is the direction (the normalised displacement field from the quenched states before and after reheating), and $\vec{s}_{ij} = \vec{s}_i - \vec{s}_j$. 

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Figure D.8 – Scatter plot $\chi_1$ as function of $\lambda_1$ for our largest gap ($\omega_c = 1.64$). $\lambda_1$ follows as $\lambda_1 = \sum_{a, \beta=1}^{3} \sum_{k, l=1}^{N} s_{ik}^a f_{lk}^{\alpha \beta} s_{k}^\beta$.

From the results in fig. D.8 we observe that at small $\lambda_1$, $\chi_1$ is independent of $\lambda_1$. Hence, we regard it as a constant. Here we estimate $\chi_1 \approx 1500$ by its median value. Note that $\chi_1$ has unit $m\omega_0^2/d_0^2$, where $m$ is the particle mass, $d_0$ is approximately equal to the inter-particle distance $a$ (hence we take $a = d_0$), and $\omega_0 \equiv 1/t_0$ is the unit frequency in our simulation which is about $\omega_D/18$. Here $\omega_D$ is the Debye frequency. Hence we get $\chi_1 \approx 1500 m\omega_0^2/a^2 \approx 4.6 m\omega_D^2/a^2$.

The relation between $\omega_D$ and $\omega_0$ is calculated by: $\omega_D = (9N/4\pi(2\omega_e^{-3} + \omega_l^{-3}))^{1/3} \approx 18\omega_0$, where $\omega_e = 1.26\omega_0$ and $\omega_l \approx 2.5\omega_e$ ($\omega_l$ is the frequency of first longitudinal modes). Note that both are plane waves. In particular, the first transverse modes consist of 12 modes and the first longitudinal modes consist 6 modes. Their identification is straightforward through the number of modes and their participation ratios, which are around 0.6. Note that $\omega_0 = 1$ in our simulation, so $\omega_D \approx 18$ and $\omega_e/\omega_D \approx 0.1$.

### D.7 Geometry of rearrangements

#### Protocol to separate rearrangements

The displacement field between the states before and after reheating may contain more than one elementary excitation. We extract them one-by-one from this displacement field, by assuming them linearly independent. This corresponds to the following algorithm:

1. Find the particle with the largest displacement.

2. Place a small sphere centred at this particle with a radius $\tilde{R}^{(i)} = (V/N)^{1/3}$ (with $i$ the increment number, starting at $i = 0$).

3. Set all displacements outside the sphere equal to zero. The particle displacements inside the sphere are not changed.

4. Minimise the energy $U$ (every particle is free to move).

5. Increase the radius of sphere: $\tilde{R}^{(i+1)} = \tilde{R}^{(i)} + \Delta \tilde{R}$, and reset the displacements as in step 3 (the particle displacements outside the sphere are set to zero and those inside the sphere equal to the original particle displacements).
D.7. Geometry of rearrangements

6. Repeat steps 4 and 5, until the localised mode is identified. In particular, stop when
\( |U^{(i+1)} - U^{(i)}| < 10^{-6} \) and, to avoid stopping too early, the norm of the displacement field is larger than \( 10^{-2} \). Note that \( U^{(i)} \) refers to the potential energy after energy minimisation, in step 4, for increment \( i \).

The local rearrangement is then the displacement field after the last energy minimisation. We then subtract it from the original displacement and continue to extract the next elementary excitation, by repeating this algorithm. We continue to do so until we have extracted all elementary excitations. In particular, we stop \( \tilde{R}^{(i)}/L > \sqrt{3}/2 \) (with \( L \) the linear size of the simulation box).

Results

Five representative samples (for two different \( K \)) showing our separation protocol are shown in fig. D.9, whereby the displacement field of each elementary excitation is plotted using a different colour. On average, we measure \( \{1.4, 1.6, 1.9, 3.5\} \) elementary excitations for \( K = \{10^2, 10^3, 3 \times 10^3, 10^4\} \) at the lowest thermal activation \( T_a = \{0.15, 0.07, 0.03, 0.03\} \) with \( t_a = 500 \).

![Figure D.9](image)

Figure D.9 – Individual local rearrangements projected on the \( xy \) plane, shown using different colours, in five randomly chosen examples (from those samples that show more than one local rearrangement) for: (top) \( K = 10^2, T_a = 0.15, \) and \( t_a = 500 \), (bottom) \( K = 10^4, T_a = 0.03, \) and \( t_a = 500 \).

We, furthermore, include the distribution of the participation ratio of the elementary excitations in fig. D.10(a), whereby the different colours correspond to the different data points in fig. 3.5(a). We observe that the elementary excitations become more localised for larger gaps. Likewise, we include the distribution of the maximum displacement of each elementary excitation in fig. D.10(b) (the different colours correspond to the different data points in fig. 3.5(b)). In this case we observe that the maximum displacement increases for our largest \( \omega_c \) (in black) as the result of string-like motion. This is supported by the distinct part of the Van Hove correlation in fig. D.10(c) that displays a sharp peak around \( r = 0 \) only for our largest \( \omega_c \) (in black). For this configuration, we plot the distribution of the number of permuting particles, \( \#n_p \), inside the ‘string’ in fig. D.10(d).
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Figure D.10 – Probability distribution of (a) the participation ratio $NP_r$ and (b) the maximal particle displacement $\max_i \|\delta \vec{r}_i\|$ at different $\omega_c$. (c) The distinct part of the Van Hove correlation normalised by the number density $\langle G_d \rangle / \rho$ at different $\omega_c$. (d) Histogram of the number of particles that permute per realisation, $#n_p$ (for largest $\omega_c$) at two different cutoff distances $r_c / d^*_0 = \{0.025, 0.05\}$. 
E appendix of chapter 4 and 5

E.1 Model detail of glasses obtained by the SWAP Monte Carlo method

Pair interaction

The soft repulsive pair interaction is:

$$\varphi (r_{ij}) = \begin{cases} \epsilon \left( \frac{r_{ij}}{R_{ij}} \right)^{10} + \sum_{\ell=0}^{3} b_{2\ell} \left( \frac{r_{ij}}{R_{ij}} \right)^{2\ell}, & \frac{r_{ij}}{R_{ij}} \leq x_c \\ 0, & \frac{r_{ij}}{R_{ij}} > x_c \end{cases} \quad (E.1)$$

where $\vec{r}_i$ is the $i$th particle’s position and $r_{ij} = |\vec{r}_i - \vec{r}_j|$. $R_{ij}$ is the non-additive particle size parameter that is defined by $R_{ij} = \frac{1}{2} (R_i + R_j) \left( 1 - 0.1 |R_i - R_j| \right)$. $x_c = 1.4$ is the cutoff distance at which $\varphi$ vanishes continuously up to third derivatives. These constraints lead to that

<table>
<thead>
<tr>
<th>$b_0$</th>
<th>-1.93601032988204</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_2$</td>
<td>-2.469400930971984</td>
</tr>
<tr>
<td>$b_4$</td>
<td>-1.07991294357375</td>
</tr>
<tr>
<td>$b_6$</td>
<td>0.160701330888951</td>
</tr>
</tbody>
</table>

The volume $V = N \bar{R}^3 / 0.58$ is fixed for a fixed $N$.

Polydispersity of the particle size parameter

The distribution of the size parameter follows

$$P(R) \sim 1/R^3, \quad (E.2)$$

where $R \in [\bar{R}, 2.22\bar{R}]$.

All these details of the model are from the “Polydisperse soft spheres” section of [150]. Equilibrium configurations are ta
E.2 \(D(\omega)\) and \(A_4\) at different \(T_p\)

The density of QLMs follows

\[
D_L(\omega) \equiv \frac{1}{3N-3} \sum_{l=1}^{3N-3} \delta(\omega - \omega_l) = A_4 \omega^4, \quad 0 < \omega < \omega_g, \tag{E.3}
\]

where \(\omega_l\) is the discrete eigen frequency of QLMs and \(\omega_g\) is the upper cutoff of this scaling regime which is 20% – 30% of the Debye frequency \(\omega_D\) [68]. \(A_4\) decreases by three orders of magnitude from \(T_p = 0.8\) to \(T_p = 0.3\). See \(D_L(\omega)\) and the values of \(A_4\) in Fig. E.2.
E.3 Non-linear modes

The non-linear modes $\vec{z}_f$ can be obtained by minimizing the cost function by applying the steepest descent method that starts from the QLMs directions. Clearly, the cost function is

$$G = \frac{|U^{(3)} \cdot \vec{z} \vec{z} \vec{z}|^2}{|H \cdot \vec{z} \vec{z}|^3}$$

[115, 143] *, where $z$ is a random vector. $G$ is proportional to the energy barrier when the system is close to the instability. The total interaction $U = \sum_i \sum_{j > i} \phi$ where $\phi$ is the pair interaction potential (see Section 1 in Chapter 4 for the definition). $U^{(3)} = \frac{\partial^3 U}{\partial \vec{r} \partial \vec{r} \partial \vec{r}}$ and $H = \frac{\partial^2 U}{\partial \vec{r} \partial \vec{r}}$ where $H$ is the Hessian matrix. $\cdot$ means the contraction. Specifically

$$H: \vec{z} \vec{z} = \sum_{i<j} \left( \frac{\phi''}{|r_{ij}|^3} - \frac{\phi'}{|r_{ij}|^4}^2 \right) \left( \vec{r}_{ij} \cdot \vec{z}_{ij} \right)^2 + \frac{\phi'}{|r_{ij}|^3} \left( \vec{z}_{ij} \cdot \vec{z}_{ij} \right)$$  \hspace{1cm} (E.4)

$$U^{(3)} \cdot \vec{z} \vec{z} \vec{z} = \sum_{i<j} \left\{ \left( \frac{\phi''}{|r_{ij}|^5} - \frac{\phi''}{|r_{ij}|^6}^3 + 3 \frac{\phi'}{|r_{ij}|^5} \right) \left( \vec{r}_{ij} \cdot \vec{z}_{ij} \right)^3 + \left( \frac{\phi''}{|r_{ij}|^3} - \frac{\phi'}{|r_{ij}|^4} \right) 3 \left( \vec{r}_{ij} \cdot \vec{z}_{ij} \right) \left( \vec{z}_{ij} \cdot \vec{z}_{ij} \right) \right\}$$  \hspace{1cm} (E.5)

The coefficients $\lambda_1, \kappa_1, \chi_1$ thus are obtained by Taylor expansion of the potential $U$ along $z_f$.

E.4 Estimation of $c_1$

We show the scatter plot of $\chi_1 a^2 / m \omega_D^2$ ($\chi_1 a^2 / m \omega_D^2$) v.s. $\omega^2 (\omega_D^2)$ for QLMs (non-linear modes) at three $T_p$. $\chi_1$ almost does not change compared to $\chi$. We thus estimate $c_1$ from non-linear modes by taking the median value of $\chi_1 a^2 / m \omega_D^2$ where $\omega_D = 14.5, 15.3, 17.7$ from high to low $T_p$. Correspondingly, $c_1 \approx 2, 3, 9$.

* $G$ does not depend on the magnitude of $z$. 

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Figure E.3 – Scatter plots of $\chi a^2/m\omega_D^2$ v.s. $\omega^2$ (left) and $\chi_1 a^2/m\omega_1^2$ v.s. $\omega_1^2$ (right). The median of $\chi a^2/m\omega_D^2$ is approximate to 0.74, 1.5, 6.0 corresponding to $T_p = 0.8$, 0.55, 0.3, respectively.
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Skills

Numerical methods: Monte Carlo, Molecular dynamics, Path integral molecular dynamics, High performance computing.

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• Nov. 20-25, 2019 Yearly Collaboration Meeting on Cracking the Glass Problem, Royaumont Abbey, France, (oral presentation included)

• Jun. 24-Jul. 6, 2019 Beg Rohn Summer School on Glasses and Jamming, Beg Rohn, France. (poster included)

• Mar. 7-8, 2019 Simons Collaboration on Cracking the Glass Problem Annual Meeting, New York, NY USA. (oral presentation included)


• Aug. 7-17, 2018 Mechanics and physics of stretchable solids, A summer school in Carglise, Corsica, France, (poster presentation included)

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