Amorphous solids manifest puzzling effects of mysterious degrees of freedom that give rise to a heat capacity and phonon scattering in great excess over what would be expected for a solid that has a unique vibrational ground state. Of particular conceptual importance is the apparent near universality of phonon scattering in amorphous solids made by quenching a liquid. To rationalise this universality, scale-free scenarios have been proposed that either hinge on there being long-range interactions between bare structural degrees of freedom or that invoke long-range criticality stemming from the emergence of marginally stable vibrational modes. In a contrasting, local scenario, the puzzling low-temperature degrees of freedom are, instead, weakly-interacting, strongly anharmonic degrees of freedom each of which involves the motion of a few hundred particles. In this scenario, the universality of phonon scattering comes about because the characteristic energy scale of the local anharmonic resonances and the strength of their interaction with phonons are both set by the glass transition temperature $T_g$, while their concentration is set by the cooperativity size $\xi$ for dynamics at $T_g$. The nanoscopic length $\xi$ is manifested in vibrational excitations of the spatial boundary of the resonances, which underlie the so-called Boson peak, and very deep, topological midgap electronic states in glassy semiconductors, which are implicated in a number of strange optoelectronic phenomena in amorphous chalcogenides. I discuss the merits of the above scenarios when confronted with experimental data.
1. Introduction

The detailed mechanism of the emergence of mechanical rigidity in structural glasses remains a disputed topic, enough so as to have found its way into the popular culture.\(^1\) This paper focuses on a specific subset of structural degrees of freedom in frozen glasses whose microscopic origin has attracted much attention since the early 1970s\(^2\)–\(^7\) and is at the heart of that debate. These puzzling degrees of freedom would not be present in solids that have a unique vibrational ground state and thus imply that structural glasses are, in fact, vastly structurally degenerate. Experimental signatures of these degrees of freedom are seen down to the lowest temperatures accessed so far in experiment – i.e. fractions of the Kelvin – thus suggesting the spectrum of the alternative structural states is truly gapless while the barriers separating such states can be arbitrarily low.

To begin discussing mechanical instabilities in low-temperature solids, we set the stage by invoking Nernst’s Law and symmetry considerations. According to the Nernst theorem, any dynamical degree of freedom, when equilibrated, must attain a unique quantum state as the temperature is lowered to the absolute zero; otherwise it must be supplanted by other degrees of freedom, for instance, by way of a phase transition. In addition to being relatively scarce, one may reasonably expect low energy states to be also relatively symmetric: On the one hand, degenerate eigenstates of the Hamiltonian comprise an irreducible representation of a symmetry group\(^8\). On the other hand, lower energy solutions of the Schrödinger equation have fewer nodes implying a progressively smaller size of the corresponding irreducible representation. Thus, the ground state is expected to be described by the totally symmetric representation. Higher energy states typically will be increasingly more degenerate and, at the same time, less symmetric.

When particles combine to form a solid, translational symmetry is drastically lowered while the (quantum-mechanical) kinetic energy is increased. A solid can not be the true ground state of the system in the absence of external field: Quantum-mechanical superpositions of degenerate symmetry-broken states are clearly lower in energy. Yet for practical situations, the tunnelling barrier that would allow the system to escape such a symmetry-broken, ‘classical’ state is incomprehensibly high\(^9\). While not being true ground states, the structures of actual solids formed on long time scales still represent low energy, relatively unique configurations. Uniqueness is important in the present context because it tautologically implies stability. Thus, solids produced as a result of very slow cooling may be expected, quite reasonably, to be both stable on every length scale and exhibit a great deal of spatial symmetry. In contrast, solids made through routes other than slow equilibration of a melt cannot be generally expected to adopt such low energy configurations or be stable at each wavelength, even if exhibiting substantial stability.
macroscopically. Nor should such hastily made solids be expected to be
periodic, implying a lack of point symmetries. Technologically important
e
eamples of strongly off-equilibrium solids are quenched glasses, deposited
films, and rubbers among many others.

This paper focuses primarily on those aperiodic solids made by quench-
ing a liquid sufficiently rapidly – via cooling or compression – so that the
liquid fails to crystallise. Instead, the particles become kinetically arrested
in a structure that is approximately a snapshot of a liquid. In reference to
window glass, which is made by cooling a silicate melt, all solids made by
quenching a liquid are also called glasses, whether transparent or not.
Judging by their strength, glasses are often rigid – despite their being
aperiodic – in some sense more rigid than many periodic crystals. It
then comes as a surprise that glasses apparently host structural degrees
of freedom whose density of states is considerably greater – at pertinent
energies – than the density of states of the vibrational modes of an elastic
medium with a unique vibrational ground state.

The discovery of these fascinating degrees of freedom came about in a
rather prosaic way [10]: At least as early as the 1960s, it became clear
that the ordinary adhesive epoxy, which is often used to affix samples in
various cryogenic experiments, conducts heat much less robustly than
does a crystalline solid. At sufficiently low temperatures, the mean free
path of a phonon in most crystals is so large that it exceeds the
dimensions of the typical sample. Under these circumstances, the heat
conductance of the sample does not scale inversely with the sample
length but is simply determined by the specific heat of the phonons,
which follows the Debye $T^3$ law [11]. On the relevant lengthscale, one
cannot even define the heat conductivity, it being a bulk property. In
contrast, epoxy – which is a glassy substance – exhibits phonon mean
free paths that are much shorter than the sample dimensions down to
very low temperatures so that its heat conductivity remains perfectly well
defined. The measured heat conductivity of glasses scales nearly quad-
ratically with temperature, viz., $T^{2-a}$, $a = 0.05 \ldots 0.2$. The latter observ-
ation became recognised relatively widely after the seminal work of
Zeller and Pohl [2] who crucially established also that the apparent
excess phonon scattering in glassy solids is accompanied by a heat
capacity in excess of the Debye $T^3$ law. This excess heat capacity scales
nearly linearly with temperature, $T^{1+a}$, $a = 0.1 \ldots 0.3$.

The presence of such a large number of residual degrees of freedom then
called for a revision of the conventional notions of mechanical stability of
solids based on a unique ground state. A simple scenario was conceived
shortly thereafter, by which the stability is compromised but only locally
and quite sporadically: Owing to the ostensive lack of local point-
symmetries on atomic lengthscales in amorphous solids, one might expect that the lattice might not be stable locally everywhere. At the same time, an amorphous solid can be regarded as isotropic on large lengthscales, the better the larger the length. One can put these two notions together by imagining small, bi-stable or, more generally, multi-stable groups of atoms that are embedded in a macroscopically stable lattice. Such a multi-stable group of atoms represents a multi-level system, but only the two lowest energy states will be relevant at sufficiently low temperatures. Thus, one arrives at the venerable two-level system (TLS) model, which is often referred to as the standard tunnelling model (STM) when the distribution of the off-diagonal matrix element \( \Delta \) is explicitly specified \([3–5,12]\). Indeed, one may make a reasonable assumption that the distributions for the on-site energy splitting \( \epsilon \) and tunnelling barrier \( V^\dagger \) each vary slowly as both quantities approach zero, as pertinent to low temperatures. One consequently obtains a unified, phenomenological description for several cryogenic anomalies observed in glasses that employs only a few adjustable parameters characterizing the number of states and the distributions of \( \epsilon \) and \( V^\dagger \)[5]. The simplest rendition of the model is a two-level system (TLS) coupled to a local dimensionless strain \( \nabla \phi \):

\[
H = \frac{\epsilon}{2} \sigma_z + \frac{\Delta}{2} \sigma_x + \sigma_z g \nabla \phi,
\]

(1)

where \( \sigma_z \) and \( \sigma_x \) are the usual Pauli matrices\([8]\). The energy density corresponding to the (single-component) deformation \( \phi \) of the lattice relative to some reference state is given in the usual fashion by \( K(\nabla \phi)^2/2 \), where \( K \) is the elastic modulus. Internal degrees of freedom cannot couple to the absolute displacement \( \phi \), hence the gradient coupling in Equation (1). Note that for the simplified, ‘scalar’ elasticity from Equation (1), there is no difference between longitudinal and transverse sound waves. We note that the tunnelling amplitude \( \Delta \) is semi-classically computed in the simplest assumption that the instanton’s motion near the tunnelling bottleneck is harmonic with the under-barrier frequency given by \( \omega^\dagger \). Thus, \( \Delta \) depends exponentially on the barrier height: \( \Delta = \Delta_0 e^{-\pi V^\dagger/\hbar \omega} \). We note that the minimalistic two-level model can be generalised by postulating a variety of soft potentials that could in principle govern the motions of small groups of atoms \([13–15]\). The greater flexibility of such models naturally allows for good fits of thermal data but at the expense of using additional adjustable constants.

The apparent two-level nature of the excess degrees of freedom was directly confirmed shortly after the model was proposed, via phonon-echo experiments\([16]\), and, much later, in single-molecule experiments that allow one to monitor the frequency of a local chromophore embedded in
a glassy matrix [17,18]. Quite tellingly, however, the latter experiments also show a deviation from the standard model. They show that quite often, a fluorescent molecule couples to what seems to be a pair of TLSs at a time or a structural resonance that has more than two levels.

In the local description, which effectively amounts to placing localised defects within a stable matrix, the concept of a (thermal) phonon seems to be still reasonably valid despite the lack of periodicity: The measured mean free path $l_{\text{mfp}}$ of a vibrational wave-packet turns out to be about hundred times longer than its wavelength $\lambda$; one can still define the frequency and wavelength sufficiently well. The macroscopic stability of the solid is thus handily ensured, too, since the “defects” are local. Since the $l_{\text{mfp}}/\lambda$ ratio gives the number of whole periods, at the pertinent frequency, that fit within the vibrational wave-packet, thus it can be thought of as a measure of how well a phonon is defined as a quasi-particle, a quality-factor of sorts. For crystals, the phonon quality factor near absolute zero can be made arbitrarily large, thus making the phonons rigorously defined excitations in the Landau sense.

Serious doubts on the local picture described above were however cast following the work of Freeman and Anderson [19], who observed that the quality factor $l_{\text{mfp}}/\lambda$ varies surprisingly little over several families of amorphous compounds; the numerical value of this ratio is close to 150. At the same time, the $l_{\text{mfp}}/\lambda$ ratio can be shown within the two-level phenomenology to be determined by the TLS density of states $\tilde{P}$ and the strength $g$ of the TLS–phonon coupling [3–5]: $l_{\text{mfp}}/\lambda \approx (\tilde{P}g^2/K)^{-1}$. Thus, one obtains that in the TLS regime, the following nearly universal relation holds:

$$\frac{l_{\text{mfp}}}{\lambda} \approx \left(\frac{\tilde{P}g^2}{K}\right)^{-1} \approx 10^2. \quad (2)$$

Similar conclusions were reached when analysing internal friction data [20], see also Refs. [21] and [22]. The above equation suggests that there is an apparent, intrinsic relationship between the material constants $g$, $K$, and $\tilde{P}$. Yu and Leggett [23] stressed that this empirical relation hardly seems a coincidence since it holds across a large set of substances exhibiting very different local chemistries which, one would think, determine local excitations.

Although the numerical value in the rhs of Equation (2) does not seem to be invariant over all known types of glassy substances, such as polymers or amorphous metallic alloys, one may still reasonably ask [20,23] how much local chemistry matters. One may even ask whether there is a way to discriminate between detailed microscopic scenarios of the origin of the excess states [24]. Is it perhaps the case that the apparent low-$T$ states in
glasses are an emergent property accompanied by a criticality induced scale invariance? A similar notion arises from a seemingly very different type of analysis, namely, the study of meanfield disordered systems in high dimensions [25]. When quenched sufficiently deeply, such systems exhibit a continuous replica-symmetry breaking (RSB), the so-called Gardner transition [26], that would naturally supply a plentitude of marginally stable modes, infinite-range correlations, and, perhaps, scale invariance in three dimensions.

Another view, espoused by Wolynes and myself [27–30], is rooted in the classical density functional theory of the glassy state itself and its origin in quenching the liquid. This picture ties the two-level systems to the molecules and their motions directly in the actual three-dimensional (3D) space. In this treatment, the rigidity of glasses emerges as a result of a translational symmetry breaking in the form of a random first-order transition (RFOT) [31,32]. In a surprisingly indirect yet natural way, the near universality in phonon scattering comes about, within this finite-dimensional framework, because of the way glasses are made. The relation between the parameters of the two-level excitations arise from experimental constraints on the rate of quenching, on the one hand, and an intrinsic connection between the cohesive energy of the solid and the interaction strength of the phonons with local degrees of freedom, on the other hand. This intrinsic connection stems from the marginal stability of small-scale motions against vibrational excitations of the lattice when the rigidity sets it. The quantum states are relatively local and turn out to be only weakly interacting at low temperatures, much as in the phenomenological tunneling model. In contrast with that model, however, the density of states of the local degrees of freedom is no longer an adjustable parameter but, instead, is rigidly prescribed by the cooperativity size for activated transport near the glass transition temperature $T_g$ and the temperature $T_g$ itself. Interactions between these emergent local degrees of freedom provide only a weak perturbation on the picture but still reveal themselves in subtle ways, such as in the otherwise strange negative thermal expansivity of low-temperature glasses [29], a conceptually important yet relatively small effect.

The three scenarios listed above are quite distinct in both style and substance. In the Yu–Leggett scenario, the mechanical stability of the overall matrix is simply assumed at the onset. The effective degrees of freedom are complex composites of local degrees of freedom interacting so strongly as to completely loose their individuality. In meanfield RSB analyses, the nature of the excitations is not entirely clear either; overall rigidity of the matrix arises internally consistently in the treatment since the kinetic barriers separating distinct aperiodic free energy minima are strictly infinite and so is the correlation length. The only explicit length
scales in the problem are the molecular length and the vibrational amplitude. The role of finite-dimensional effects, such as fluctuation-induced lowering of the symmetry breaking transition is not obvious. At the same time, perturbative analyses suggest such effects could completely destroy the transition in three dimensions [33].

In the RFOT-based approach, in contrast, there is a finite – and a substantial indeed – temperature range, in which the barriers are finite, thus allowing for reconfigurations of finite-sized regions, the cooperativity length $\xi$ not exceeding a few nanometers. The system is mechanically stable on lengths less than $\xi$ but is metastable on larger lengthscales. The scenario explicitly describes how the vast majority of strongly interacting molecular translational degrees of freedom in the uniform liquid become frozen out with lowering the temperature so that the remaining degrees of freedom can be regarded as relatively local and only weakly coupled. Along with the emergence of a finite length scale $\xi$ there come about very special degrees of freedom that are simply not accessible to meanfield treatments: Vibrations of the boundary of a reconfiguring region reveal themselves as an additional, vibrational-like contribution to the total density of states widely known as the Boson peak [28,29]. The latter is an umbrella term referring to degrees of freedom seen by vibrational spectroscopies at frequencies near 1 THz and has been also associated with the 'bump' in the heat capacity and the so-called plateau in the heat conductivity [5,28,29]. The plateau is characterized by significantly enhanced phonon scattering, relative to the two-level regime but not quite to the point of complete phonon localization. The term ‘Boson’ refers to the linear temperature dependence of the peak’s strength. Now, under certain circumstances, which can be argued to be realised in glassy semiconductors [34,35], the boundaries of reconfiguring regions also can host very special electronic states of topological origin. All of these predictions are borne out in experiment, thus providing crucial support for the local description in many experimental situations.

This paper is organised as follows. The scenario of Yu and Leggett is discussed in Section 2. Section 3 covers the picture based on the RFOT theory. The marginal stability scenario is discussed in Section 4. The final Section 5 provides a summary of the main points and touches upon possible experimental ways to differentiate between the various microscopic scenarios that have been put forward.

2. Yu–Leggett scenario

In this section, I review the main points of the Yu–Leggett scenario. To set the stage, we note that the Green’s function of a massless field $\phi$ governed by the energy function $K(\nabla \phi)^2/2$, in $d$ spatial dimensions, is given, up to a
numerical factor, by the expression $1/Kr^{d-2}$, see, for instance, Section 5.7.5. of Ref. [36]. Thus, two elementary degrees of freedom described individually by Equation (1) and located, respectively, at $r_i$ and $r_j$, will be effectively coupled via a 'dipole–dipole' interaction

$$J_{ij} \sim (g_i \nabla)(g_j \nabla)/Kr^{d-2} \sim g^2/Kr^{d}_{ij},$$

(3)

up to a geometric factor reflecting the ‘orientation’ of the couplings $g$ and the space dimensionality $d$:

$$J_{ij} \sim d^{d}_{ij} \propto \Gamma(d/2 - 1)\pi^{-d/2}d(d - 2),$$

(4)

see Equation (5.110) of Ref. [36]; $\Gamma$ is the standard gamma function. Note the $g$’s are vectorial for the scalar elasticity $K(\nabla\phi)^2/2$ but must be rank-two tensors in a proper treatment [37,38]. For the sake of argument, we adopt the following functional form in three spatial dimensions:

$$J_{ij} \sim \frac{J}{r_{ij}^3},$$

(5)

where

$$J = \frac{g^2}{K}.$$  

(6)

Suppose a macroscopic quantity of the elementary low-energy anharmonic local degrees of freedom are embedded in a macroscopically stable lattice. To avoid excessive repetition, we shall interchangeably call these residual degrees of freedom ‘elementary,’ ‘bare,’ or ‘primitive.’ Two such primitive degrees of freedom $i$ and $j$ will form a resonance so long as their on-site energy difference is less than $J/r_{ij}^3$. The latter coupling strength will also determine the level spacing in such a resonance. At equilibrium below temperature $T$, all resonant pairs separated by a distance shorter than distance $r_T$ determined by

$$k_B T \sim J/r_{T}^3,$$

(7)

will be found largely in their quantum ground state, or thermodynamically ‘frozen-out.’ The *kinetics* of this ‘freezing-out’ are not explicitly considered in this analysis but could substantially affect measured quantities since measurements are performed on finite timescales. Thus, below a temperature $T$, the equilibrium concentration of thermally active resonant pairs is limited from above by the quantity $1/r_{T}^3$ implying an upper bound on the specific heat

$$c(T) \leq T/J$$

(8)
This can be restated as a bound on the density of states:

\[ n(E) \lesssim \frac{1}{J}, \]  

(9)

cf. Ref. [23]. As just mentioned, the inequality in the above equations reflects the uncertainty as to the spatial arrangement of the resonant pairs, a notion we will return to shortly. Perhaps more importantly, the inequality reminds us that the argument is not entirely constructive: While it predicts a bound on the effective density of strongly interacting degrees of freedom, it is agnostic as to whether or why such degrees of freedom should be present in the first place.

An improved estimate for the effective density of states of the compound resonances was obtained by Yu and Leggett [23] who noted that the energy \( E \) of a resonance will be statically broadened as a result of freezing-out of those resonances exceeding \( E \) in energy by the amount

\[ \Delta E \simeq \left| \sum_j J_{ij} \right| \simeq \rho_b \left| \int_{r_{\min}}^{r_{\max}} dr^3 \frac{J}{r^3} \right| \]

(10)

\[ \simeq J \rho_b \ln \left( \frac{r_{\max}}{r_{\min}} \right) \]

(11)

\[ \simeq J \rho_b \ln \left( \frac{E_{\max}}{E} \right), \]

(12)

where \( \rho_b \) is the number density of the individual degrees of freedom and the energy of a compound resonance is determined by \( E \simeq J/r^3 \) as before. The ultraviolet cut-off energy \( E_{\max} \) should correspond to the closest spacing between individual elementary degrees of freedom. The resulting density of states \( \rho_b/\Delta E \) is, then:

\[ n(E) \lesssim \frac{1}{J} \ln^{-1}(E_{\max}/E). \]

(13)

The above ideas were implemented systematically by Burin and Kagan, [39] see also Refs. [40] and [41]. Note also that the logarithmic correction could potentially explain rather effortlessly – even if not fully quantitatively – why the heat capacity and conductivity should deviate from the simple linear and quadratic dependences, respectively.

Thus, Equation (9) – or its more accurate counterpart (13) – provides an upper bound for the amount of instability in any solid, a surprisingly simple yet apparently very general result. What are physical implications of this general result? Substituting

\[ \bar{P} = \frac{1}{J} \]

(14)
in the ratio in the first equality in Equation (2) and using Equations (6) and (9), one obtains a lower bound on the \( (l_{mfp}/\lambda) \) ratio for phonons:

\[
l_{mfp}/\lambda \approx 1.
\]

This condition is exactly the venerable Ioffe–Riegel criterion [42], which prescribes that in order to define semi-classically a quasi-particle, its mean free path must be greater than its wavelength. We note that a regime \( l_{mfp}/\lambda \approx 1 \) is in fact observed across all glassy substances in a broad temperature range [19]. (This range may not seem broad on log-log plots [19] but in fact, covers the major portion of the temperature range that is ordinarily studied below the glass transition.)

The upper bound on the density of states of the compound resonances in Equations (9) and (13) evidently becomes much less useful at very low, sub-Kelvin temperatures. In this regime, this upper bound exceeds by a factor of \( 10^2 \) or so the apparent density of states actually observed in experiment, cf. Equation (2). Recently, Vural and Leggett [24,43] have presented calculations suggesting this issue may not be a ‘deal-breaker’ but instead may only be a quantitative one in that it seems to be satisfactorily resolved, if one explicitly specified that the individual degrees of freedom be multi-level systems. Specific molecular realisations of such multi-state resonances have been proposed by Schechter et al. [44–46], in a variety of systems such as disordered films of interest to quantum computing[47]. One way to see how the ‘multi-levelness’ affects the physics is to note that the couplings \( J_{ij} \) between the primitive degrees of freedom will generally scale with the square of the number of levels while scattering of individual phonons scales only linearly with that number.

In the Yu–Leggett scenario, the final density of states from Equations (9) or (13) does not depend on the detailed nature of the individual elementary degrees of freedom or even on their concentration \( \rho_b \). The latter concentration only determines the threshold ultraviolet energy below which the universality sets in: The larger the concentration \( \rho_b \), the higher the energy threshold. Yet there is a potential issue posed by the type of density of states in Equations (9) and (13): It does not explicitly depend on the material’s particle density! To appreciate why this is problematic, imagine the atoms were twice larger in size while the coupling constant \( J \) from Equations (6) did not change. Clearly one now expects a density of states that is eight times lower, in contradistinction with Equations (9) and (13). Although the elastic constants and other material constants are likely correlated with the atomic size – which makes the preceding argument somewhat delicate – the correlation is certainly not strict: A brief inspection of a table of elastic moduli, for instance, reveals the moduli vary within two or more orders of magnitude for conventional solids even
though the atomic size varies only within 50% or so. To summarize, the correct scaling of the density of states in the Yu–Leggett picture with the material density would be recovered only if there is a strict correlation between the coupling constant $g$ and the elastic constant $K$ that involves the atomic size $r_a$:

$$g^2 = CKr_a^3,$$

(16)

where $C$ is a constant of dimensions energy that is not expressly determined by the atom size.

Another potential complication has to do with the spatial arrangement of the primitive degrees of freedom. Indeed, suppose for the sake of argument the latter degrees of freedom were to comprise a periodic lattice characterised by a perfectly spatially uniform nearest neighbour distance. If taken at its face value, the argument leading to Equations (9) and (13) suggests one would run out of resonance-capable pairs above a certain, relatively short length and, hence, below a certain energy. For instance, spin systems defined on a periodic lattice have a gapped spectrum, or, if spin waves are present, they exhibit a $T^{3/2}$ heat capacity at low temperature. In contrast, the spectrum in Equation (13) is significantly richer at low energies. Of course, the couplings are expected to be random in glasses, but how strongly random? In the extreme case of couplings being distributed randomly around zero, we expect that the effective molecular field acting on an individual degree of freedom is no longer determined by the $J_{ij}$ themselves, as in Equation (10), but instead by their mean square values [48,49]. The integral over $J^2 \propto 1/r^6$ is perfectly infrared convergent, thus obviating the argument.

One way to include effects of the spatial arrangement of the primitive degrees of freedom would be to reformulate the argument leading to Equations (9) and (13) in the reciprocal space. We have seen that to avoid a gap in the density of states of the resonances, it is imperative that the bare degrees of freedom do not comprise a strict lattice. Instead their concentration must exhibit deviations from the strictly periodic or uniform spatial arrangement down to the lowest wavevector $q$. The magnitude of such deviations on the length scale $r \sim 1/q$ is given by the structure factor of the system: $S(q) \equiv (1/N) \sum_{ij} e^{iq(r_i-r_j)}$. In view of $E \sim Jq^3$, one obtains

$$n(E) \approx S[(E/J)^{1/3}] \frac{1}{J},$$

(17)

where we have omitted the logarithmic correction from Equation (13) partially because the rate of change of the structure factor at relevant energies well exceeds that of the logarithm and partially for simplicity.
We note that $S(q \to \infty) \to 1$ thus recovering the high energy asymptotics from Equations (9) and (15).

The low energy asymptotics are more interesting. In the $q \to 0$ limit, the structure factor is determined by the typical magnitude of density fluctuations (p. 313 of Ref. [32]) and, hence, by the compressibility: $S(q \to 0) \to \rho k_B T/K$ where $\rho$ is the particle density. Since the structure of the glass is largely arrested below the glass transition temperature $T_g$, except for some ageing and subtle changes related to a decrease in the vibrational amplitude, we thus obtain:

$$P \lesssim \frac{\rho k_B T_g}{K} \frac{1}{J}.$$  

(18)

Note the above expression now does contain the material’s density, but, seemingly, at the expense of universality. Recall, however, that by the equipartition theorem, $K\langle(\nabla \phi)^2 \rangle = k_B T$. At the same time, the relative displacement $\langle|\nabla \phi|\rangle$ corresponds with the typical vibrational displacement $d_v$ relative to the particle spacing $a$: $\langle|\nabla \phi|\rangle = d_v/a$. Therefore we have

$$\left(\frac{d_v}{a}\right)^2 \simeq \frac{\rho k_B T_g}{K},$$

(19)

leading to

$$P \lesssim \left(\frac{a}{d_v}\right)^2 \frac{1}{J}.$$  

(20)

The ratio $d_v/a$ is bounded from above by and numerically close to the ratio $d_L/a$, where the quantity $d_L$ is the so-called Lindemann displacement, i.e. the vibrational displacement at conditions where mechanical rigidity sets in. Numerically, $d_L/a \simeq 0.1$ almost universally in the physical three dimensions, which is the venerable Lindemann criterion of melting [50,51]. Thus, at sufficiently low temperatures,

$$\frac{l_{mfp}}{\lambda} \simeq \left(\frac{g^2}{JK}\right)^{-1} \left(\frac{a}{d_L}\right)^2 \simeq 10^2,$$

(21)

nearly universally, in view of Equation (6). The formula above requires that the phonon scattering be resonant. This affords one an internal consistency check within the Yu–Leggett scenario, since the condition for resonant scattering, $r_T < \lambda$, implies the ‘weakly-dampened’ regime in Equation (21) can be observed at temperatures such that:

$$k_B T \simeq (k_B T_D a)^{3/2} / J^{1/2},$$

(22)
where $T_D$ is the Debye temperature and we used Equation (7). Since $r_T \geq a$, one obtains a very reasonable upper bound

$$J < k_B T_D a^3 \Rightarrow E_{\text{max}} \simeq k_B T_D,$$

up to a numerical factor of order one. Leggett [20] pointed out that Equation (22) defines a temperature below which the interacting defects can be thought of as Ising-like spins, because resonant exchange of phonons allows for flip–flip processes, while above that temperature, the model is more Heisenberg-like.

Thus, we observe that a microscopic picture of a macroscopically stable amorphous solid, in which strongly interacting local anharmonic degrees of freedom form resonant, spatially extended pairs appears to be internally consistent. The density of states of the resonances drops by a factor of $10^2$ or so once their spatial extent significantly exceeds the molecular length. In both high and low energy limits, the $l_{\text{mfp}}/\lambda$ is nearly universal and numerically close, respectively, to $10^0$ and $10^2$. The appearance of the ratio $(a/d_L)^2$ in the low-energy part of the density of states (21) is significant: In modern theories of liquid-to-solid transitions [32], this ratio plays the crucial role of the order parameter for translational symmetry breaking. Its magnitude is of order $10^2$ in solids but changes discontinuously to zero in the liquid. It is reassuring that Equation (20) automatically implies no frozen-in degrees of freedom could be present in a uniform liquid. Finally note the above argument can be reformulated in all dimensions $d \geq 3$. The $(a/d_L)$ ratio is expected to increase linearly with the space dimensionality [52]:

$$\frac{a}{d_L} \propto d,$$

while the coupling constant increases combinatorially rapidly with $d$, as remarked just below Equation (4). Consequently, the numerical value of the lower bound (21) quickly decreases to the overdamped value of 1 even for dimensions only modestly exceeding the physical value 3. This limits the usefulness of this lower bound on the $l_{\text{mfp}}/\lambda$ ratio for putative high-dimensional solids. In any event, the Yoffe–Riegel bound in Equation (15) reminds one of the original Einstein’s view on solids as collections of uncorrelated oscillators, while heat transfer is carried out by short wave packets [53], a view we now recognise as meanfield. Note that according to Equation (10), the interaction volume is determined the system’s volume itself. In this sense, the interactions are infinite-range.

Despite its generality, the infinite-range scenario is agnostic as to whether the bare, local degrees of freedom should be present in the first place. While this lack of being constructive may seem an attractive feature
of the argument, it does call for some vigilance. Indeed, there are plenty of amorphous materials that either do not exhibit detectable TLS-like degrees of freedom, such as freshly deposited silicon films or where the amount of two-level systems seems to depend on preparation [6,54,55]. (Nevertheless, such films progressively develop an excess of local resonant degrees of freedom when annealed, in the absence of crystallisation.) By construction, the density of states for the bare degrees of freedom should be higher than that prescribed by Equation (17). Conversely, a set of local degrees of freedom characterised by the DOS from Equation (17) would not form resonances. [56] Next we turn to a scenario that does describe on a constructive basis just how local degrees of freedom could emerge in an aperiodic solid made by a quench of an equilibrated liquid.

3. The mosaic scenario and its quantization

We first review select notions of the non-meanfield scenario of how mechanical rigidity emerges in structural glasses that is provided by the random first order transition (RFOT) theory. An up-to-date and very extensive, pedagogical account of the RFOT theory [32] as well as an older, less technical review [31] are available. A recent article [57] expands those notions established for molecular systems to a greater variety of preparation protocols so as to include amorphous collections of particles such as jammed colloidal particles or granular assemblies.

The RFOT theory generalizes some established, quantitative notions of the liquid-to-periodic-crystal transition. The latter transition represents the extreme case where the translational degrees of freedom freeze out all at the same time in a first-order transition, thus leaving in essentially no degrees freedom other than lattice vibrations. Important and interesting exceptions to this notion include solids that are largely periodic but that still house strongly anharmonic structural excitations such as phasons [58], orientational dynamics in relaxor ferroelectrics [59], or proton transport in solid ice [60], to name a few.

What makes liquid-to-solid transitions difficult for analytical treatment is that they are intrinsically, strongly discontinuous, thus rendering power-law expansions for small values of the order parameter mathematically dangerous. The necessity for the discontinuity itself was elegantly argued for by Landau [61], who showed that a liquid-to-solid transition could be continuous at most in one isolated phase point. Brazovsky showed decades later that if such a critical point existed, it would be pushed down to absolute zero by fluctuations [62,63]. Moreover, Bernal [64] made a much less formal yet equally insightful notion that the entropy of a liquid can be presented as a sum of translational and vibrational entropy – a view
justified for covalently bonded liquids [32] – implying crystallisation always exhibits latent heat.

Early attempts at developing quantitative theories of periodic crystallisation by Kirkwood and others [65] followed a Landau-like approach and employed, as order parameters, expansion coefficients in front of the Fourier components of the solid’s density profile. A non-vanishing coefficient in front of a non-zero $q$ Fourier component means translational invariance is broken. These attempts achieved much conceptual progress [66] but being limited to only a few Fourier components for technical reasons, fell short of producing a quantitative theory. A technical breakthrough in the field was achieved when a different density ansatz for the solid was adopted, viz., a sum of Gaussians:

$$\rho(r) = (\alpha/\pi)^{3/2} \sum_i e^{-\alpha(r-r_i)^2},$$  \hspace{1cm} (25)$$

where the summation is over the vibrationally averaged positions of individual particles. Note this ansatz would be exact for a strictly harmonic solid comprised of equivalent particles [67,68].

A class of non-perturbative density functionals were subsequently found that happen to sum an infinite subset of diagrams [69] and that quantitatively reproduce the phase behaviours of hard spheres and soft particles alike [70]. In these approaches, the optimal value of the order parameter $\alpha$ is found variationally, by optimising the free energy $F(\alpha, \bar{\rho})$ with respect to both $\alpha$ and the average density $\bar{\rho}$. Felicitously, the uniform liquid is also described by the density ansatz (25) if one sets $\alpha = 0$, thus allowing one to build an effective free energy function that applies to both phases and, significantly, to the inter-phase transition state. The order parameter $\alpha$ changes its value from zero to $10^2/a^2$ following crystallisation, a discontinuous transition indeed. A non-zero value of $\alpha$ implies that each atom is now subject to an effective confining potential in the form of an Einstein oscillator. The analysis can be extended, in periodic crystals, to small deformations around vibrational ground states and thus can be used to test for mechanical stability in a broad range of wavelengths. Note that the value of $\alpha$ near the saddle point of the free energy $F(\alpha, \bar{\rho})$ corresponds with the inverse square of the vibrational displacement near the stability limit: $\alpha \simeq 1/d^2_L$, up to a numerical constant of order one (cf. Equation 21).

In an equally quantitative fashion, it has been shown that a generic aperiodic lattice can be metastable with respect to the uniform liquid, whether it is made of hard or soft particles [51,71,72]. When aperiodic metastable minima of the free energy functional emerge, the free energy excess of a specific individual minimum over the uniform liquid ensemble is typically around $k_B T$ per particle. At the same time, the number of
distinct individual aperiodic minima scales exponentially with the system size, $e^{s_c N/k_B}$, where the quantity $s_c$, called the configurational entropy, is numerically close to $k_B$. Indeed, the excess entropy of a liquid relative to the corresponding crystal is empirically known to be about $1.5k_B$ per atom or larger near melting [73]. That the free energy deficit of an individual free energy minimum is compensated by the entropic stabilization due to the multiplicity of the minima implies that the totality of the distinct aperiodic structures could be just as stable as the uniform liquid. Computation of the configurational entropy for actual liquids is difficult but has been accomplished relatively recently for model liquids within the replica-symmetry breaking (RSB) framework [74]. The latter framework has an important methodological dividend: The totality of all metastable structures described by the ansatz (25) automatically turns out to have the same free energy and total entropy as the uniform liquid. (This is similar to what is seen in a variety of related spin-models [75].) Therefore, the sole fact of emergence of metastable aperiodic minima automatically implies that the minima correspond with equilibrium configurations. To contrast aperiodic crystal formation from the ordinary liquid-to-crystal transition, the emergence of the degenerate aperiodic solids has come to be called a random first order transition (RFOT). As just mentioned, the entropy of the liquid is a smooth function of the temperature; thus unlike the transition to a periodic crystal, the RFOT has no latent heat.

The emergence of transient rigidity predicted by the RFOT theory – in the form of long-lived local structures – immediately explains the established experimental fact that below a certain temperature (or above a certain density), transient cages form around each molecule already in an equilibrated liquid as directly seen, for instance, in neutron scattering [76] where one finds an extended plateau in the intermediate scattering function; the Debye–Waller factor of a transiently trapped particle can be directly measured and is numerically close to what it would be in a perfectly stable solid. The lifetime $\tau$ of the cage can be arbitrarily long – only subject to one’s patience – and ultimately determines the viscosity $\eta$ of the liquid according to [77–79]:

$$\eta \approx \mu \tau,$$

originally due to Maxwell; $\mu$ is the high-frequency shear modulus. In addition to the aforementioned plateau observed in neutron scattering experiments, the formation of transient cages leads to other consequences that have been observed, such as the violation of the Stokes-Einstein relation or decoupling of translational and rotational diffusion, and decoupling of dielectric and mechanical relaxation (see Refs. [68,78], and [80] and references therein). Microscopic arguments indicate this transient
ergodicity breaking is a soft crossover occurring near viscosities of order $10^1 - 10^2$ Ps [81,82], see Figure 1, a result consistent with experiment. At this viscosity, the activation energy of transport begins to grow rapidly. The crossover, whose ballpark temperature we denote with $T_{cr}$, becomes a sharp transition in the meanfield limit. The temperature of the latter meanfield transition is often denoted with $T_A$[52,75], or the dynamical temperature $T_d$.

Thus, we arrive at a seeming conflict: On the one hand, the free energy of the liquid below the crossover is locally minimised by a spatially non-uniform density profile (25) with $\alpha \simeq 10^2$, where the site locations $\{r_i\}$ now correspond with an aperiodic lattice. On the other hand, the liquid flows, thus eventually restoring the translational symmetry and implying that $\alpha = 0$ on long times. How can one have it both ways at the same time with regard to the value of $\alpha$?

The situation is indeed somewhat subtle, but actually does not present a contradiction. To appreciate this, imagine first an individual, small, and isolated ferromagnetic domain sufficiently below the Curie temperature of
the bulk material so that the domain maintains its magnetisation long
enough for the observer to notice and measure it, but not too long so that
the polarization of the domain will typically flip before the observer runs
out of patience. (Magnetic recordings deteriorate exactly because of such
flips.) Thus, on the one hand, the free energy is minimised in one of the
two polarised states: The ratio of the duration of the flip (i.e. the instanton
time) to the typical wait time inside a minimum can be made arbitrarily
small. On the other hand, the average magnetisation is still zero and the
symmetry is maintained but only on very long times. Now imagine a
macroscopic magnet below the Curie point, but not too much much
lower, and assume for convenience that the magnet was cooled so that
the average magnetisation is small, much lower than what it would be in a
fully polarised sample. Clearly, the sample will represent a ‘mosaic’ of
regions polarised up or down. The so polarised domains are separated by
domain walls. The number, extent, and shape of the walls will depend on
the mismatch penalty between the distinct polarisations, translational and
vibrational entropy of the walls, etc. The mosaic is not static because of the
non-vanishing translational and vibrational entropy of the domain walls.
Thus for long times, the magnetisation of the sample as a whole and any of
its regions will be zero on average. At the same time, the free energy of the
sample is minimised by polarised solutions, not the paramagnetic solution!

Figure 2. Partial graphical summary of some of the physics associated with the mosaic picture
of an equilibrated glassy liquid below $T_c$. The quantities $a$, $d_L$, and $\xi$ stand, respectively, for
the lattice spacing, the particle displacement at the mechanical stability edge, and the
cooperativity length for structural reconfigurations. The intrinsic uncertainty in the position
of the boundary can be thought of as vibrations of the domain wall encompassing the
reconfiguring region; these vibrations account for the Boson peak [28]. The tension of the wall
has a contribution from special midgap electronic states that are present, if the material
exhibits spatially varying bond saturation [34,35].
Likewise, a liquid can be thought of as a mosaic made of distinct free energy minima when $\alpha > 0$ [83,84], see a graphical summary of ensuing phenomena in Figure 2. However, in contrast with the ferromagnet, which has only two distinct free energy minima to speak of, the liquid has exponentially many such minima. In this case, the lengthscale of the mosaic is determined much less by the entropy of the domain walls than by the multiplicity itself of the minima. Calculations [85] suggest the multiplicity of the minima dominates the pertinent physics for values of the configuration entropy that exceed already the very small value of $10^{-4}k_B$ per particle. Sufficiently below the temperature when the minima begin to form, local interconversions between the minima can be considered as rare events so that their rates can be accurately estimated using the venerable transition state theory [86,87]. Specifically, the free energy cost of locally replacing the existing configuration by another, equivalent aperiodic configuration can be presented as a sum of two contributions [83]:

$$F(N) = -T_s N + \gamma N^{1/2},$$

(27)

where $-T_s$ is the bulk driving force and the odd-looking term $\gamma N^{1/2}$ approximates the mismatch penalty between two distinct aperiodic free energy minima. The scaling of this mismatch penalty is slower, in dimensions three or higher, than the $N^{(d-1)/d}$ scaling expected for interfaces between two distinct thermodynamic phases. This reduction comes about because a strained region separating two equivalent aperiodic minima can typically lower its energy by as much as $\sim N^{1/2}$ by locally replacing any region by yet another equivalent random structure [83,84,88,89]. Appropriately, the resulting stabilisation of the interface scales with the magnitude of Gibbs free energy fluctuations of an individual minimum [83,88] and is thus approximately determined by the bulk modulus of the material [32,88]:

$$\gamma \approx (Kk_BT/\rho)^{1/2}.$$  

(28)

This and other available detailed estimates for the coefficient $\gamma$ yield values for relaxation barriers in glassy liquids that agree well with experiment [84,88,90,91], without using any adjustable parameters. The kinetic barrier corresponding to the free energy profile (27),

$$F^\ddagger = \gamma^2 / 4k_B T_s,$$

(29)

is finite unless the configurational entropy vanishes. This barrier directly determines the rate at which the liquid will flow when sheared, by virtue of

$$\tau^{-1} = \tau_0^{-1} e^{-F^\ddagger / k_B T}$$

and Equation (26). The quantity $\tau_0$ is a vibration
timescale numerically close to a picosecond \([92]\). The critical size corresponding to the profile (27),

\[
N^\frac{1}{2} = (\gamma/2Ts_c)^2,
\]  

(30)
is finite and obligingly becomes greater than the molecular size \(1\) below the crossover temperature \(T_{cr}\) \([57,81]\), Figure 1(b), consistent with the premise that each individual particle is confined to a cage. One may further ask: What is the size \(N^*\) of a region that will have reconfigured once the critical size \(N^\frac{1}{2}\) is reached? The reconfiguration size \(N^*\) is an important quantity because it corresponds with the lengthscale of the mosaic and determines the cooperativity length for activated transport. To answer the above question, we first recall that in the expression (27) for the free energy cost of reconfiguring \(N\) particles, the energy reference is set at zero, \(F(N = 0) = 0\). An equally likely configuration of the same sample but with a region of size \(N^*\) flipped is thus determined \([27,84,88,93]\), by a non-vanishing solution \(N^*\) of the equation \(F(N)|_{N = N^*} = 0\). The quantity \(N^*\) therefore gives a lower bound for the size of a region that can be occupied by a single aperiodic minimum \([27,93,94]\). In fact, it is also the typical size occupied by a single solution since beyond \(N^*\), there is a non-vanishing probability that yet another solution will be present in the region: \(-F(N)|_{N > N^*}/k_BT > 0\). Equations (27) and (28) yield straightforwardly

\[
N^* = \frac{\gamma^2}{Ts_c} = \frac{K}{\rho k_B T(s_c/k_B)^2}.
\]  

(31)

To gain an additional perspective on this result, one may recall the expression for the particle-number fluctuation in a uniform liquid \([67]\):

\[
\delta N = (N\rho k_BT/K)^{1/2}\].
\]

This means that the lower bound on the size \(N^{(1)}\) of a region which will routinely accommodate for adding/removing one particle, \(\delta N = \pm 1\), is given by \(N^{(1)} = K/\rho k_BT\) (cf. the second equality in Equation 31). Yet this type of ‘free volume’ \([95]\) mechanism for mass transport is irrelevant for systems with broken translational symmetry such that the density profile is given by Equation (25), \(\alpha \simeq 10^2\). Under the latter circumstances, the liquid can no longer flow and so creation of free volume would require creating a vacancy. The latter would cost many multiples of the thermal energy \([96]\), \(\sim Ka^3 \simeq ak_BT \simeq 10^2k_BT\) (cf. Equation 19), and thus occurs very rarely. The cooperativity length for creating a vacancy would be strictly infinite, by Equation (31), since disallowing motions other than vibrations implies \(s_c = 0\).

Now, in three dimensions the physical length corresponding to the cooperativity size \(N^*\) is given by
The cooperativity size $N^*$ depends algebraically on the barrier and, hence, only logarithmically on the relaxation time. Indeed, Equations (29)–(32) yield:

$$N^* = \left(\frac{\xi}{a}\right)^3 = \frac{\left(4 F^4/\gamma\right)^2}{16 k_B T \rho K \ln^2(\tau/\tau_0)}. $$

(33)

Because the timescale for conventional quenches varies between seconds and hours while $\tau_0 \approx 10^{-12}$ s, we conclude that the cooperativity size is apparently nearly universal for routinely made glasses. Numerically, this size is about $200$ [27,84,88,90,91], implying

$$\left(\frac{\xi}{a}\right) \approx 6, \text{ at } T = T_g. $$

(34)

For speedier quenches, the cooperativity size $N^*$ can be made significantly smaller than 200, but probably no smaller than a few tens of particles, see Ref. [97] and also the discussion of cooling protocols in Section 4. Since the molecular size $a$ corresponds with the size of a rigid molecular unit, or ‘bead,’ [81] which typically measures several angstroms across [81,97], the cooperativity length $\xi$ reaches only a few nanometers in magnitude at the glass transition. This is consistent with indirect observations using several types of non-linear spectroscopy [98–100] as well as direct observation of cooperative reconfigurations on the surface of metallic glasses [101]. We note that the cooperative reconfigurations amount to a dynamic, not static heterogeneity. To detect dynamic heterogeneity, one must measure a four-point correlation function, which is not accessible to linear spectroscopy. Conversely, no easily describable static structural patterns would be obvious on the length scale $\xi$ [102], see however below for possible electronic signatures.

To estimate the absolute values of $a$ and $\xi$ – as opposed to the dimensionless ratio $\xi/a$ – one must be able to identify the effective particle of the theory, i.e. the bead. Rigid molecular units are straightforwardly identified in molecular substances; the corresponding size matches well its value as determined by calibrating the entropy of fusion of the substance by that of a Lennard–Jones like substance [81]. Such chemical determination however becomes ambiguous in covalently bonded liquids such as the chalcogenide alloys. Very recently, Lukyanov and Lubchenko [97] (LL) have designed a chemically inspired algorithm to generate ensembles of octahedrally coordinated amorphous structures that turn out to reproduce consistently the first sharp diffraction peak (FSDP) in the structure factor. The FSDP is viewed by many as reflecting the so-called medium-range order in glasses and has been a subject of debate for decades [103–106].
have argued that the lengthscale underlying the FSDP is, in fact, the bead size. Thus, the basic notions of the RFOT theory can be connected directly with actual substances while allowing one to obtain estimates for absolute values of the reconfiguration length and barrier \cite{88,91}. Generically \cite{32},

\[
1/\xi^3 \simeq 10^{20}\text{cm}^{-3},
\]

i.e. one domain per several hundred atoms.

Thus, Equations (27)–(30) mathematically embody a key physical notion regarding the emergence of mechanical stability in aperiodic solids: The material is stable on a finite length scale \( \xi \), which meaningfully exceeds the molecular length, while larger regions are only metastable, the escape barrier given by Equation (29). Thus, the question of the mechanical stability of the system is that of quantifying the latter escape barrier. According to Equations (29) and (32), the reconfiguration barrier and extent both increase with cooling because the configurational entropy, as any entropy, must decrease with temperature. A very good empirical fit is given by the functional form \cite{107}

\[
s_c = \Delta c_p(T_g)T_g(1/T_K - 1/T) \\
\propto (T - T_K), \quad T \to T_K,
\]

where \( \Delta c_p(T_g) \) is the heat capacity jump at the glass transition. The resulting temperature dependence of the relaxation barrier and cooperativity length are exemplified in Figure 1.

The stability of aperiodic structures made by quenching a liquid is thus achieved not because such an aperiodic state is strictly unique, in contrast with ordinary crystalline solids, but because the alternative states are behind sufficiently high barriers and their number is sufficiently small. How stable are glasses? At the glass transition achieved using a routine quench, \( \tau/\tau_0 = e^{F_z(T_g)/k_BT_z} \simeq 10^{15} \). At a temperature half as large as \( T_g \), the corresponding relaxation time would be \( \tau/\tau_0 = e^{2F_z(T_g)/k_BT_z} \simeq 10^{30} \), a monstrously large number. In reality, relaxation in frozen glasses occurs toward states that are stabilized enthalpically relative to the frozen-in states and is much faster than that implied by the naive estimate above \cite{93}. Nevertheless, the relaxation times for ageing in deeply quenched glasses are still astronomically large \cite{93}, consistent with the everyday experience that glasses are often mechanically harder than periodic crystals, even if at the expense of being brittle.

The emergence of the degenerate aperiodic crystal characterised by the density profile (25) is largely driven by steric repulsion \cite{32}; lower
temperature and/or increase in pressure is simply a means to increase density. Elastic response, at non-zero frequencies, then arises self-consistently: It can be shown straightforwardly that \( \alpha \) is equal to the shear modulus of an individual aperiodic minimum, up to a numerical constant determined by the Poisson ratio [68]. The large value of order parameter \( \alpha \) (\( \alpha a^2 \approx 10^2 \)) explains, in retrospect, why perturbative treatments of liquid-to-solid transitions are mathematically difficult. The corresponding, small vibrational amplitude \( 1/\alpha^{1/2} \) thus can be regarded as the key emergent quantity in the problem. Appropriately, this emergent (small!) length scale readily arises in meanfield and non-meanfield treatments alike. Because each individual reconfiguration must occur just at the mechanical stability edge for the moving atom – so as not to compromise the stability of the lattice – the length scale \( 1/\alpha^{1/2} \) also has the clear physical meaning [84] of the displacement of an individual particle during a reconfiguration: \( d_L = \alpha^{-1/2} \). This notion also formally enters in RSB treatments [74,108] because two replicas are considered distinct if their overlap, which is basically a Debye–Waller factor of sorts, is less than a certain value.

The lengthscale \( \xi \), on the other hand, is intrinsically non-meanfield; it arises only because of the locality of interactions. It turns out the latter non-meanfield effects undergird the great majority of the dozens of quantitative predictions the RFOT theory has made, see reviews in Refs. [31] and [32]. Of particular significance in the present context are the quantum-mechanical consequences of the special physics associated with the length \( \xi \), which are often overlooked, perhaps because the translational symmetry breaking \( \alpha = 0 \rightarrow \alpha > 0 \) that occurs as a result of the random first order transition is entirely of a classical origin for most substances known. (Some interesting new physics could appear for helium [109] or electrons!) Here we highlight several features that have been reviewed previously in Refs. [32] and [110] and, in addition, some more recent results.

To quantise the structural excitations of a frozen solid that is a mosaic of aperiodic free energy minima, we first enquire about the classical density of states of such a solid just above a kinetic glass transition at a temperature \( T_g \). The word ‘kinetic’ implies that there are still lower energy states that would have been available in principle to the system, if it had been cooled more slowly. Nevertheless, the system became kinetically arrested in an off-equilibrium configuration because the cooling rate was greater than the inverse relaxation time of a subset of the translational degrees of freedom. If, on the other hand, no lower-energy states were available, then the glass transition would be truly thermodynamic. The putative lowest energy aperiodic state is often called the ideal, Kauzmann state [111]. Now, the smallest reconfigurable region has exactly one state available near \( T_g \). (As far as the corresponding reconfiguration is concerned, the surrounding
matrix is by construction regarded as purely elastic.) Thus, with regard to the latter region, the temperature \( T_g \) corresponds to a thermodynamic glass transition. A general form of the density of states for such a system, at low energies, is \( \Omega(E) \propto \exp[E/k_B T_g + O(E^2)] \), where the ground state is at \( E = 0 \) by construction. The glass transition formally comes about because in a finite temperature range \( T \in [0, T_g] \), the integrand of the partition function \( \int dE \Omega(E) e^{-\beta E} \) is dominated by the vicinity of \( E = 0 \). That is, the system freezes into its ground state already at the finite temperature \( T_g \). This formally corresponds to a density of states \( \Omega(E) = (1/k_B T_g) \exp(E/k_B T_g) \), the prefactor needed to reflect that exactly one ground state is found at energy \( E = 0 \) or below: \( \int_{-\infty}^{0} dE \Omega(E) = 1 \).

Considering that at any given time the spatial concentration of regions that can reconfigure is \( 1/\xi^3 \), one obtains that the total density of states due to the domains is

\[
n(E) \simeq \frac{1}{k_B T_g \xi^3} e^{E/k_B T_g}.
\]  

(37)

Thus, without explicit consideration of the kinetics of structural excitations accessible at cryogenic temperatures, the above expression yields for the density of states of low energy excitations: \( \tilde{P} = 1/k_B T_g \xi^3 \), since \( T_g \) of most glasses is much larger than liquid helium temperatures. Substituting specific values for the glass transition temperature and bead size \( a \) yields \( \tilde{P} \simeq 10^{45\pm1} \text{m}^3\text{J}^{-1} \). This value is consistent with experiment [21].

In addition, optimising the phonon part of the TLS + phonon energy function, \( \sigma_z g \nabla \phi + \int d^3 r K(\nabla \phi)^2/2 \), with respect to the displacement yields \( \sigma_z g / a^3 = -K \nabla \phi \). Multiplying this by \( \nabla \phi \), recalling that \( \langle K(\nabla \phi)^2/2 \rangle = k_B T/2 \) by equipartition, and noting that \( |\langle \sigma_z \nabla \phi \rangle| \simeq |\nabla \phi| \), one obtains

\[
g \simeq (K k_B T/\rho)^{1/2},
\]  

(38)

cf. Equations (16) and (28). According to the discussion leading to Equation (16), the above expression satisfies the basic requirement that the density of states scale inversely proportionally with the atomic volume. The mutual resemblance of Equations (28) and (38) is also notable and, in fact, is far from coincidental: The quantity \( \gamma \) from Equation (28) can be thought of as reflecting the strength of intrinsic structural fluctuations while \( g \) reflects the response to an externally imposed perturbation in the form of a structural defect.

In view of Equation (38), the interaction between the cooperative reconfigurations becomes
\[ J \simeq k_B T_g a^3, \tag{39} \]
i.e. comparable to the upper bound on the coupling strength between the bare degrees of freedom in the Yu–Leggett scenario (cf. Equation 23). Despite this circumstance, the effects of interaction (39) are much less important in the presently discussed local scenario because the local degrees of freedom are distributed broadly in terms of their energy spacing, the distribution width being on the order of \( k_B T_g \), Equation (37). Thus, the high value of the laboratory glass transition, relative to the coupling between the local degrees of freedom, is the reason why these degrees of freedom could form at best isolated resonant pairs, if any at all.

Now, combining Equations (37) and (38) readily yields an expression for the quality factor of the phonons \([27,29]\):

\[
\frac{l_{\text{mfp}}}{\lambda} \simeq \left( \frac{\xi}{a} \right)^3 \simeq 10^2. \tag{40} \]

We used the numerical value \( 10^2 \) that specifically pertains to the routine laboratory quench of a molecular substance, as discussed following Equation (33).

Thus, we observe that at the purely classical level, the density of states is set jointly by the glass transition temperature and by the cooperativity size \( \xi \) of the ‘mosaic.’ The resulting prediction is consistent with experiment, Equation (2). The corresponding heat capacity and conductivity are then predicted to be, respectively, strictly linear and quadratic in temperature, at cryogenic conditions. At the same time, the phonon ‘Q-factor’ \( l_{\text{mfp}}/\lambda \) is determined by the particle content \( N^* \) of the cooperative volume. The latter volume is not strictly universal but depends logarithmically on the quench speed, by Equation (33). Thus, one can obtain rather generally:

\[
\frac{l_{\text{mfp}}}{\lambda} \simeq \left( \frac{\xi}{a} \right)^3 \simeq 16 \left( \frac{d_L}{a} \right)^2 \ln^2 (\tau_g/\tau_0), \tag{41} \]

where we used Equation (19) and \( \tau_g \) is the time scale of the glass transition. Note that the above result does not explicitly depend on space dimensionality \( d \). The dependence is only implicit, through the Lindemann ratio \( d_L/a \). The formal reason for the lack of dimensionality dependence is the lack of explicit dependence of the mismatch penalty term \( \gamma N^{1/2} \) on the space dimensionality. Interestingly, the Lindemann ratio enters into the above expression in the exactly reciprocal fashion to Equation (21). In view of Equation (24), we obtain that for a fixed timescale of the glass transition, the phonon quality ratio in Equation (41) decreases quadratically with space dimensionality, that is, not nearly as rapidly as what is prescribed by the formula (21). Thus in sufficiently many dimensions and fixed \( \tau \), the
RFOT-predicted density of states can be very much lower than the upper limit from Equation (21). This is just another way to see that the emergence of the finite length scale $\xi$ hinges crucially on the ability of the liquid to reconfigure, below the crossover to activated transport, on time scales that are attainable in the sample preparation.

Quantum dynamics does enter into the problem of determining the density of states explicitly when one estimates the density of tunnelling states properly so as to account for the ability to carry out the reconfigurations at low temperatures. To make such an estimate one must consider the classically defined microcanonical density of states simultaneously with the distribution of the tunnelling barriers separating those states, all at a temperature just above $T_g$. In the early part of the century, Lubchenko and Wolynes (LW) \cite{27,29} provided detailed calculations for this quantum effect within the RFOT framework. Here we only point out that the density of configurational states of our generate aperiodic solid is indeed exponentially large: $e^{s/N/k_B}$, thus implying that not only is it possible to find an alternative state at lengthscale $\xi$, but it is also possible to find a state reachable from the existing configuration by following an essentially barrier-less path on a lengthscale that exceeds $\xi$ only modestly. In volumetric terms, the cooperativity size for such zero-barrier events is only about 10% larger than for a reconfiguration with a typical barrier \cite{27,29}. Finding zero-barrier paths requires exploring a somewhat larger region than the typical reconfiguration size. The corresponding motions are thus rare and thermodynamically cannot undermine the mechanical stability near $T_g$. These tunnelling events through extraordinarily low barriers require concerted motion of several hundred particles. The coherence is generally suppressed owing to friction, since the tunneling event couples to local elastic modes. According to Refs. \cite{27} and \cite{29}, damping becomes particularly important already at temperatures comparable to the frequency of the under-barrier motion near the top of the barrier. The top-of-the barrier frequency turns out to be essentially a fixed fraction of the Debye frequency $\omega_D$:

$$\omega^\dagger \simeq 1.6(a/\xi)\omega_D,$$  

see also Ref. \cite{92}.

Including quantum-tunnelling dynamics in the treatment preserves the basic scaling of the density of states (37) with $T_g$ and $\xi^3$ but introduces significant multiplicative corrections and requires use of an adjustable parameter to fit the heat capacity all the way from cryogenic temperatures to the high temperature set by $k_BT = \hbar \omega^\dagger$. Including only the two lowest energy states in the treatment now yields, up to a multiplicative factor, a
time-dependent heat capacity owing to the distribution of finite tunnelling times. For large times, the theory yields [29]
\[
\lim_{t \to \infty} C(t) \propto t^{c/2} T^{1+c/2},
\]
where the constant \( c = \hbar \omega^3/\sqrt{2} T_g \) is numerically less then 0.1. The weak time dependence in Equation (43) is consistent with the long time behaviour of the experimentally observed heat capacity [115–118]. The heat capacity in the laboratory also exhibits a mildly superlinear temperature dependence, but the deviation from strict linearity predicted by this argument is smaller than what is seen in experiment. We note that the same approximate arguments [29] that yield the expression (43) also imply that the heat conductivity is mildly super-quadratic in temperature. In contrast, the experiment seems to yield a mildly sub-quadratic dependence.

The problem of the deviation of thermal conductivity from the simplest prediction is handily resolved, nevertheless, after one realises that the presence of the lengthscale \( \xi \) introduces additional physics reflected in a new sort of excitation. For one thing, a proper calculation of the density of states for a region of finite size must account for zero-point vibrations of its boundary! Thus, an internally consistent treatment must include the vibrational excitations of the domain wall separating cells in the (quantised) mosaic. We [28,29] have called these excitations ‘ripplons’ to distinguish them from ordinary vibrations of a stable lattice. Although behaving in many ways like ordinary vibrations – the intensity of the vibrations goes linearly with \( T \) – the ripplons are not simply localised linear vibrational modes of a mechanically stable lattice but, instead, correspond to excited states of a structural resonance whose potential energy surface is bistable or multistable. (The surface is multi-dimensional, of course, since \( N \approx 10^2 \) particles are involved in reconfigurations.) Despite this strongly anharmonic aspect of rippon motions, their frequencies can be straightforwardly estimated, if one ignores damping effects due to their interaction with phonons. These modes can be labelled by spherical harmonic quantum numbers, if we assume the reconfiguring region is roughly spherical. The mode frequencies are then a simple combination of the Debye frequency and the dimensionless domain size \( (\xi/a) \):
\[
\omega_l \approx 1.34 \omega_D (a/\xi)^{5/4} \sqrt{(l-1)(l+2)/4}
\]
\[
\approx 0.15 \omega_D \sqrt{(l-1)(l+2)/4}.
\]
(44)

Here \( l \geq 2 \). The second equality is obtained when we use the value of \( \xi \) corresponding to a routine quench as in Equation (40). The curious scaling \( (a/\xi)^{5/4} \) is modestly different from the \( (a/\xi) \) scaling expected on geometric
grounds because of the effective curvature dependence of the mismatch penalty in Equation (27).

The frequencies from Equation (44) fall right within what is called the Boson peak range. When these excitations are included along with the two-level excitations, the resulting predictions for the heat capacity and conductivity match the experiment well, without using any adjustable parameters, see Figures 3 and 4. The predicted heat conductivity is not strictly monotonic in the plateau region, an effect not apparent in experiment. This is likely a result of ignoring ripplon–ripplon interactions in the theory. A simple parameterisation of damping effects due to such interaction readily improves agreement with experiment, but at the expense of using an adjustable parameter [29].

We see that a constructive treatment of the anharmonic motions characterised by an intrinsic length scale $\xi$ of the mosaic dictates that there must be a significant density of states near the plateau frequencies. The resulting description explains in a unified fashion two sets of seemingly separate cryogenic anomalies: On the one hand, the approximately linear excess heat capacity and the nearly universal phonon scattering at sub-Kelvin temperatures are seen as being caused by the lowest-energy subset of excitations of these local structural resonances. On the other hand, accounting for the high-energy, ‘ripplonic’ part of the spectrum of the local resonances already at the simplest level quantitatively accounts for the excess specific heat and phonon scattering at the plateau temperatures.

![Figure 3.](image)

**Figure 3.** The bump in the amorphous heat capacity, divided by $T^3$, as follows from the derived TLS + ripplon density of states [29]. The theoretical curves correspond to different values of the glass transition temperature relative to the Debye temperature, the effects of friction increasing with $T_g/T_D$. The thick solid line is experimental data for a-SiO$_2$ from Ref. [115]. (For a-SiO$_2$, $k_BT_g/h\omega_D \simeq 4.4$.)
Lubchenko and Wolynes, Section V of Ref. [29], have outlined steps for a more proper way to quantise the mosaic, so as to account for both the repulsion between the classically obtained energy levels and the effective renormalization of individual tunnelling amplitudes due to the rest of the tunnelling motions. That discussion indicates that the diagonal and off-diagonal elements of the tunnelling centres, such as the quantities $C_{15}$ and $\Delta$ from Equation (1), are in fact correlated, in contrast with standard treatments. The resulting distribution [29] of $\epsilon$ and $\Delta$ is no longer factorisable; it now has two relatively distinct contributions. One contribution comes from highly quantum TLS, whose classical energy splitting $\epsilon$ is effectively pinned near zero. The other contribution comes from those TLS that more closely resemble the prescription of the standard tunneling model. This predicted dichotomy between highly quantum and quasi-classical structural resonances would seem to explain the apparent existence of ‘fast’ and ‘slow’ tunnelling systems noted early on by Black and Halperin [120]. The ‘fast’ two-level systems would account for the surprisingly fast onset of heat capacity – faster than that predicted by the STM – seen in experiment. Also in an improvement over the results from the purely quasi-classical analysis, the density of states – once corrected for the effects of level repulsion and the renormalisation of tunnelling amplitudes – becomes weighted more heavily toward higher energy, consistent with the mildly

**Figure 4.** Heat conductivity [29] corresponding with Figure 3, in comparison with two experimental curves. The (scaled) experimental data are taken from Ref. [119] for a-SiO$_2$ ($k_B T_g/\hbar \omega_D \simeq 4.4$) and Ref. [19] for polybutadiene ($k_B T_g/\hbar \omega_D \simeq 2.5$). The low-$T$ portion is parametrised according to $l_{mfp}/l = 150$, Ref. [19], while the plateau region is computed without using adjustable parameters.
sub-quadratic temperature dependence of the heat conductivity seen in the laboratory.

A rather exotic yet consequential manifestation of the ripplons is that, together with the underlying structural transition, they are predicted [29] to quantitatively account for the negative thermal expansivity seen in many glasses [121]. The idea is that the phonon-mediated dispersion forces between thermally active local resonances effectively squeeze the sample. This squeezing is entirely analogous to the Casimir effect between plates in a vacuum, but with the phonons filling in for the photons. The quantity of such thermally active local resonances grows sufficiently fast with temperature so as to counteract the intrinsic propensity of solids to expand with temperature owing to the asymmetry of near-neighbour inter-particle interactions. The present author is not aware of any attempts to rationalise the unusual negative thermal expansivity within any other theoretical frameworks. Although a negative Grüneisen parameter [11] is not uncommon in complex crystalline solids, its common appearance in amorphous materials – which are isotropic down to very short lengths – seems rather surprising. In my view, the natural emergence of a negative thermal expansivity in this picture lends it substantial support.

Additional support for the quantum mosaic picture came relatively recently from a somewhat unexpected direction: Zhugayevych and Lubchenko have argued [34] that in some substances with correct atomic orbital structure, the domain walls separating distinct aperiodic minima should host special, very deep midgap electronic states analogous to the solitonic midgap states in trans-polyacetylene [122]. Specific, quasi-1D molecular motifs were generated where the midgap state is centred around an over-coordinated or under-coordinated atom [35]. More generally, such midgap states are expected to reside on interfaces between distinct states of charge-density waves [123]. The deep midgap states have many interesting properties: They display a reverse charge-spin relation. A half-filled state, which has spin 1/2, is electrically neutral while the filled and empty states are, respectively, negatively and positively charged but nevertheless spinless. Exactly such states appear to be present in amorphous chalcogenides: Pristine samples exhibit a relatively clean absorption edge and show no detectable ESR signal. Yet after being exposed to macroscopic quantities of photons at near-gap frequencies, these chalcogenides manifest a simultaneous increase in midgap absorption and number of unpaired spins [124,125]. Both the number of midgap absorbers and the number of unpaired spins seem to saturate at $\sim 10^{20} \text{ cm}^{-3}$. This density is in remarkable agreement with the RFOT theory-based estimate for spatial concentration of the domain wall regions, Equation (35). The figure $\sim 10^{20} \text{ cm}^{-3}$ is interesting in that it is significantly greater than the typical concentration.
of dopants in crystalline semiconductors. It is remarkable that a material could host such large quantities of what seems to be intrinsic ‘defects’ – which become apparent upon irradiation – while not being amenable to conventional doping[126].

Already in 1975, Anderson [127,128] proposed his negative-$U$ model, which postulates effective attraction between electrons residing on a relatively localised orbital. The model provides an elegant mechanism for efficient pinning of the Fermi level near the middle of the forbidden gap, viz., at the energy where a singly occupied centre would be. Because of the negative Hubbard’s $U$, the defect states are typically filled and are optically active but at supra-gap frequencies. Anderson speculated already in 1975 that the putative negative-$U$ physics may be related to the TLSs, a prescient insight indeed. Yet the interactions responsible for the effective electron-electron attraction on a particular site would be present at every site. As such, these interactions would also determine the stabilization due to

---

**Figure 5.** Top: The electronic density of states of an amorphous sample of As$_2$Se$_3$ obtained in Ref. [132] using the structure-building algorithm developed in Ref. [97]. A very deep midgap state is visible, whose wavefunction is shown in the bottom panel, alongside the wavefunctions of two select states near the edges of the two mobility bands. The acronym ‘B3LYP’ in the top panel signifies the specific quantum-chemical approximation [137–140] used to obtain the electronic spectra. Image courtesy of Dr. A. Lukyanov.
forming a filled valence band and hence the value of the forbidden gap itself [129]. This circumstance makes the applicability of the negative-U scenario to chalcogenides questionable. The gap in the chalcogenides, crystalline or amorphous, is largely due to the charge density wave arising from the spatial variation in both bond strength and local electronegativity [123,130]. In contrast to the original negative-U proposal, the midgap states in the picture advanced by Zhugayevych and Lubchenko are robust for topological reasons [131]. This robustness comes about because malcoordination cannot be removed by small lattice deformations, but only by breaking/creating a bond or recombination of opposite malcoordinations. Like in the original negative-U model scenario, there is still some stabilisation of a filled state, however the strength of stabilisation is not directly linked to the gross chemical interactions that determine the gap size. Instead, the stability has to do with relatively subtle polarisation effects occurring when an electron (hole) is added to a radical. Several specific bonding configurations can be argued to be stabilised by the addition of electrons/holes to neutral defects already using simple ideas à la G. N. Lewis [35]. Recently, bulk samples of amorphous chalcogenides exhibiting such midgap states have been computationally generated [97]. According to Ref. [132], not only do these computationally generated samples appear to host both the mobility-band and the associated Urbach tail [133–136] of localised states, but they also exhibit just the type of topological states that were predicted by the ZL picture. The electronic spectrum of the sample and the wavefunction of the midgap state are exemplified in Figure 5.

Finally we point out that at temperatures below but not too much below the crossover to the activated transport, the cooperative reconstructions are less compact and are supplemented by a different type of motion that is locally string-like [82]. These motions correspond to transient opening of the local cages and have been argued to make a universal contribution to the so-called Johari–Goldstein [141], or β-relaxation [142]. From the string viewpoint, the transition from the aperiodic solid $\alpha>0$ to the uniform liquid $\alpha=0$ can be thought of as a string-deconfinement transition, in which string-like motions percolate ultimately resulting in molecular translations becoming barrier-less [82]; we will return to this important notion shortly. We note that other, system-dependent local motions can be present in glassy materials, such as conversions between rotamers in branched polymers.

4. The global marginal-stability scenario

A rather distinct-looking explanation for low-$T$ universalities in glasses has grown up in recent years within strictly meanfield, replica symmetry breaking (RSB) treatments of the structural glass transition. In a
fascinating set of developments [25,143–146], the latter treatments indicate that for a sufficiently deep quench within a specific free energy minimum, the local motions within their cages themselves would eventually exhibit marginal stability and, subsequently, will undergo further symmetry breaking in the form of a continuous phase transition. This transition is formally analogous to the infinite step RSB found in the Sherrington–Kirkpatrick model [147] and also more pertinently to the Gardner transition in $p$-spin models [26,148]. To make direct connections among the problems of the glass transition, jamming, and a variety of packing problems [149], it is often convenient to consider not only thermal quenches at constant pressure, but also pressure quenches at constant temperature. The two types of quenches are straightforwardly related for strictly rigid particles, whose equation of state contains the pressure and temperature in the combination $p/T$. For rigid spheres, the density $\rho$ and volume fraction $\phi$ can be used interchangeably.

To describe the Gardner transition, we first recall that meanfield-theory liquids – similarly to Potts spin glass and $p$-spin models – exhibit a one step RSB at some temperature $T_A$ (or pressure $p_A$), which corresponds with the emergence of a thermodynamic quantity, $e^{k_B T}/k_B$, of equivalent free energy minima. In meanfield theory, each minimum becomes separated from the rest of the minima by strictly infinite barriers; the structure corresponding to each minimum is aperiodic. The transition signifying the emergence of this complex free energy landscape is depicted by the $(\phi_A, 1/p_A)$ point in Figure 6.

Figure 6. The phase diagram of a meanfield liquid in the $(\phi, p^{-1})$ plane, after Ref. [25]. The quantities $\phi = \rho/(\pi\sigma^3/6)$ and $p$ are the filling fraction and pressure, respectively, $\sigma$ the diameter of the sphere. EOS = equation of state. Note reports on the location of the low-$\phi$ end of the Gardner line vary [143].
Suppose now one quenches a liquid starting from a state with $\alpha > 0$, i.e. when a liquid is already securely arrested in one of those equivalent, infinitely deep aperiodic free energy minima. As the quench continues further, a Gardner transition occurs eventually \([144]\), where the current free energy minimum splits into two basins. The distinct free energy sub-basins that emerge in this way have a distributed degree of similarity; the RSB is now continuous \([113]\). The instability leading to this continuous RSB points to a rather subtle vibrational property of (high-dimensional) aperiodic solids whose detailed nature is not entirely understood at present. Here we point out that the continuous RSB implies that there is an additional contribution to the system’s entropy, in the form of the mixing entropy of the distinct replicas. The corresponding degree of freedom is an exchange of particles between replicas. The appearance of marginally stable modes on the approach to the Gardner instability, following a deep quench, may have intriguing microscopic implications. Indeed, since the Gardner transition is a critical point, it has been conjectured that the resulting scale invariance could potentially explain the universality of the cryogenic anomalies this article has focused on. In seeming support of this suggestion, Gardner-like instabilities accompanied by long correlation lengths are observed in simulations of polydisperse hard sphere liquids, where particle-swap moves are explicitly allowed \([25]\). On the other hand, analogous simulations of polydisperse soft spheres to not seem to show long range correlations, while the instabilities are rather localised and only sporadic \([150]\).

Recent arguments by Lubchenko and Wolynes \([57]\), which go beyond meanfield theory, nevertheless indicate that the implications of the Gardner scenario for actual glass-forming substances made of atoms are only limited. (To avoid confusion, we note that amorphous solids comprise a broad class of assemblies of particles ranging from chemical substances to jammed colloidal suspension to heaps of grains.) Some of the results of LW’s non-meanfield analysis are graphically summarised in Figure 7. In fundamental distinction from meanfield approaches, in which relaxation barriers are infinite by construction, LW \([57]\) discuss quenches of particulate assemblies at a finite rate. Two distinct physical situations are ordinarily realised depending on the magnitude of the dimensionless kinetic pressure, $p/k_B T \rho$ of the particle assembly. For molecular glassformers, this kinetic pressure is about four orders of magnitude larger than the ambient pressure \([32]\), being numerically in the Gigapascals or higher. Defining such a kinetic pressure relies on the particles’ possessing an effective rigid core. This is an excellent approximation for atoms at normal pressures, which do exhibit a relatively rigid ionic core. This is because exciting electrons out of the core requires energies much exceeding the thermal energy. The kinetic pressure is nearly completely counterbalanced
by the cohesive interactions between the atoms; the difference is comparable to the atmospheric pressure, of course. Now, the time interval between inter-particle collisions is very short in such systems, significantly less than a picosecond and so vibrational equilibration is very quick. Thus, even if subjected to the fastest quench realisable in a laboratory, such a system will undergo the translational symmetry breaking \((\alpha = 0) \to (\alpha \approx 10^2)\) while still equilibrated. Further quenching results in a rapid increase in the relaxation times, as discussed in Section 3. Once the rate of the slowest motions in the liquid matches the quench rate, a kinetic glass transition takes place; the system falls out of equilibrium and now follows a non-equilibrium equation of state, in which the configurational entropy is approximately steady: \(s_c = \text{const}\). These off-equilibrium equations of state are indicated by thin dashed lines in the high-density, blue sector on the diagram in Figure 7. After falling out of equilibrium, the quench will proceed approximately along a configurational adiabat \(s_c = \text{const} > 0\).

Figure 7. The off-equilibrium diagram of a non-meanfield liquid in the \((\rho, p^{-1})\) plane, where \(\rho\) is the number density. \(s_c\) stands for the configurational entropy. Liquid states cannot exist to the right of the \(s_c = 0\) line, by construction. Note that the ‘string spinodal’ is a crossover, not a sharp boundary, in view of the limited spatial extent of aperiodic free energy minima in finite dimensions.

Now suppose the effective rigid core of the particles does not significantly decrease in size with pressure (as it actually does for real molecules!). In that case, the quenched state can become arbitrarily higher in Gibbs free energy than does the closest packing of the particles: \(\Delta G = \int^V dp\). Expression (27) for the free energy cost of reconfigurations can be generalised for situations where the initial state is off-equilibrium so that the driving force now includes an enthalpic component \([57,93,151]\). The resulting relaxation represents ageing. At high pressures, the total driving force per unit volume, \(\approx \Delta G/V\), scaling approximately with the
external pressure, can thus be made arbitrarily high in the $p \to \infty$ limit. A detailed calculation [57] shows that despite the mismatch penalty also increasing with pressure, the cooperativity size for relaxation can become arbitrarily small as the pressure increased, while the corresponding reconfiguration barrier saturates at a fixed value. Physically this means that the system becomes unstable with respect to one-particle ageing events that destroy the cage that had been formed by the particle’s nearest neighbours as a result of the breaking of the translational symmetry during the formation of the aperiodic crystal.

The cage-escape events are locally string-like, see Figure 8(a). The strings will generally emanate from multiple locations and percolate, thus resulting in zero-barrier relaxation events and partial restoration of translational symmetry. These notions are entirely analogous to the microscopic picture put forth some time ago by Stevenson, Schmalian, and Wolynes [82] in the context of the equilibrium crossover between activated and collisional regimes in finite dimensions. The reader is reminded that the position of this equilibrium crossover is much lowered relative to the

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**Figure 8.** (a) A stringy instability is signalled by the ability of a particle to escape the cage via a displacement that significantly exceeds the vibrational magnitude. The vibrational amplitude in the direction of lower pressure exceeds its typical value, while the collision frequency is lowered. (b) Illustration of how compression of an anisotropic cage can lead to a local symmetry breaking upon which the caged particle will be subject to a bistable effective potential and will have to choose one of the minima upon further compression, while leaving the remainder of the cage slightly undercoordinated.
meanfield spinodal at $T_A \left( p_A \right)$ where metastable minima in the liquid just begin to form but are easily overcome by thermal fluctuations [81]. LW argued [57] that a similar instability would take place in quenched glasses as well, with the difference that relaxation is now also downhill in the free energy of an individual aperiodic minimum and thus results in structures that are significantly stabilised enthalpy-wise.

A separate argument [57] which is related to the string argument, but is somewhat different in spirit – suggests that a milder instability can occur in systems of particles at pressures that are not quite as high as those required for the string-instability to occur. Here one notices that owing to the inherent lack of symmetry in the immediate coordination shell of a particle in an aperiodic lattice, the cages formed around each particle are anisotropic. Thus, sufficiently strong compression can lead to a situation where for a particle located close the centre of its cage, the number of contacts it makes with its immediate neighbours could decrease below the minimum number of constraints needed for mechanical stability, see Figure 8(b). According to Maxwell [152], this number is equal to $2d$ in $d$ spatial dimensions. Accordingly, this unstable configuration must separate two configurations each of which may be metastable. Further compression will result in the particle having to choose one of the metastable configurations, while the vacant end of the original cage will partially collapse, or ‘buckle.’ Instabilities of a similar type have been also discussed by Wyart et al. [153–155].

The emergence of two new metastable configurations from one is a symmetry breaking. Because this symmetry breaking results in further stratification of the free energy landscape that emerged at the equilibrium crossover, it can perhaps be thought of as a finite-dimensional realisation of the Gardner transition. Whether this is case is not clear since buckling could cause further relaxations; complete analysis of this possibility is presently lacking. In any event, for the buckling instability to take place, the difference between the particle displacements along the long and short axes of the cages must exceed the amount a bond can deform under the pressure in question. This notion may be relevant to the aforementioned lack of divergent correlations in simulations of soft particles [150]. In the context of actual glassformers, one may further conclude that buckling would be efficiently suppressed by quantum effects [57].

Thus at a first glance, the string-spinodal and the buckling instabilities represent candidates for the emergence of marginal stability in finite-dimensional systems with potential implications for the emergence of anharmonic degrees of freedom in cryogenic glasses. Yet already for rigid spheres, qualitative estimates [57] indicate that to reach these instabilities, one must achieve kinetic pressures that are multiples of the kinetic pressure the atoms exert on each other at normal conditions.
Ordinary, thermally quenched glasses are nowhere close to this regime, of course. In addition, any incipient criticality due to such instabilities would be destroyed by the activated reconfiguration events that occur by ageing because at a critical point, relaxation times strictly diverge \[36\] whereas the activation time remains finite and, in fact, decreases with pressure on approach to the string spinodal \[57\]. This is entirely analogous to the way the criticality due to mode-mode coupling kinetic catastrophe at the meanfield transition at temperature \(T_A\) is destroyed by the activated transitions \[52,81,83\].

It seems instructive to make an explicit connection between the LW arguments and Yu–Leggett philosophy. It is possible to estimate the coupling between the putative Gardner degrees of freedom exemplified in Figure 8(b). For the sake of concreteness, we will work with rigid particles implying enthalpy changes come from pressure variation, at constant temperature: \(dH = Vdp\). The amount of lattice distortion along the \(y\)-axes gained over the displacement \(\alpha_y^{-1/2}\), relative to the typical in-cage displacement \(\alpha_x^{-1/2}\), is equal to \((\alpha_y^{-1/2}/\alpha_x^{-1/2})\nabla \phi\). The resulting enthalpy bias gives the coupling of the transition to the displacement field: \(g \approx pa(\alpha_x/\alpha_y)^{1/2}\). Further recalling that the bulk modulus for rigid particles goes as \(K = k_B T \rho (p/k_B T \rho)^2\) \[57\], we obtain:

\[
g \approx (\alpha_x/\alpha_y)^{1/2}(Kk_B T/\rho)^{1/2}, \quad (45)
\]

consistent with Equation (38). Indeed, during string-like motions that occur near the crossover, particle displacement in one direction significantly exceeds displacements along the other directions. This can be formally viewed as the ratio \((\alpha_x/\alpha_y)^{1/2}\) greatly exceeding 1. Such degrees of freedom would interact with each other much more strongly than do the modes in a bona fide aperiodic crystal, in which \(\alpha_x \approx \alpha_y\), thus resulting in their ready freezing-out.

We observe that since for the Gardner modes, \(\alpha_y^{-1/2}\) does not exceed \(\alpha_x^{-1/2}\) by much, their energetics are similar to the energetics of the local structural reconstructions reviewed in Section 3. The basic energy scale for the density of states is determined by the only pertinent energy scale in the problem, viz., the pressure at the Gardner transition, times the particle volume. This is numerically similar to the temperature at the beginning of the quench and thus is quite analogous to the local scenario from Section 3. Likewise, the infinite-range mechanism of the universality from Section 2 will not apply here because of the lack of resonance between the Gardner modes.

Finally, we briefly comment on the amorphous solids made by quenching a liquid starting from a configuration on the low-density side of the
string-spinodal in Figure 7. Such quenches would be typical for colloidal suspensions whose ‘molecular’ time-scale $\tau_0$ is much larger, easily by 10 orders of magnitude, than that in molecular liquids proper. This is because the microscopic time scale $\tau_0$ is now determined by the solvent’s viscosity and the (very large) particle size. LW [57] argued that rigidity emerges in such colloidal-particle assemblies following the crossing of the string-spinodal at a point that is far away from equilibrium. Under these circumstances, local regions will undergo zero-barrier relaxation events leading to the emergence of activated dynamics in those regions, possibly followed by avalanches. Because of the large value of $\tau_0$, even the smallest barrier will result in the relaxed region being virtually rigid. The rigid regions formed in this way will percolate resulting in a jammed solid. Although very interesting in their own right, such jammed solids are essentially classical, because of the large particle mass. This large mass would altogether prevent observing the presently discussed quantum anomalies in jammed solids.

5. Summary and experimental tests going forward

We have reviewed a number of ways to think about the quantum-mechanical freezing out of the liquid degrees of freedom in glassy solids as they approach absolute zero. These ‘relics’ of liquid motions amount to a substantial density of states in excess of the Debye-like vibrational degrees of freedom that reveals itself in the form of resonances at sub-Debye frequencies.

The Yu–Leggett scenario, Section 2, postulates the existence of some bare degrees of freedom that are not explicitly specified. Despite this agnosticism, one may generate a criterion for mechanical stability with respect to compound excitations involving motions of several bare degrees of freedom that interact. This analysis then yields a meaningfully restrictive upper bound on the density of structural states is excess of the vibrational motions of a fully stable solid, at least in the physical three dimensions. These excess structural excitations are viewed as resonances formed by the bare degrees of freedom; the spatial extent of the resonances can be arbitrarily large, yet it is lower than the wavelength of thermal phonons, thus enabling these compound degrees of freedom to scatter phonons resonantly. There appear to be two distinct scattering regimes. At low temperatures, where the thermally pertinent interaction range between the bare degrees of freedom significantly exceeds the molecular length scale, phonons have a relatively high fidelity, $l_{\text{mfp}}/\lambda > 10^2$. As the temperature is raised, the system crosses over to a regime characterized by complete phonon localization, $l_{\text{mfp}}/\lambda > 1$. We saw that for the spatial...
dimensionality greater than the physical value of 3, even the low-\(T\) bound on the \(l_{\text{mfp}}/\lambda\) ratio quickly drops to the Yoffe–Riegel value of 1, thus limiting the usefulness of this bound for estimating the actual amount of phonon scattering.

The scenario advanced in Section 3, using the RFOT theory, is more concrete about the origin of TLSs. In that approach, the lifetimes of metastable, transiently rigid local structures are explicitly computed, alongside the corresponding reconfiguration size. The experimentally observed, gradual onset of rigidity in the classical regime is quantitatively reproduced. This gradual onset of rigidity is associated with the growth of the size \(\xi\) of mechanically stable regions and the activation barrier for structural reconfigurations. The value of this cooperativity size \(\xi\) near the glass transition – where the liquid falls out of equilibrium – along with the glass transition temperature itself, then determine the gross density of states of the residual liquid motions that have not frozen out as a result of the glass transition but that now must equilibrate quantum mechanically at low temperatures. Further quantum effects have been analysed and lead to improvements in the estimate of the density of states and time dependence of the specific heat. In the LW scenario, the phonon ‘quality’ ratio \(l_{\text{mfp}}/\lambda\) is determined by the size of the cooperative region \((\xi/a)^3\), which is predicted by the RFOT theory; it depends on the quench speed weakly, logarithmically, thus pegging it near the value of order \(10^2\) for glasses made by conventional quenches. The finite, even if relatively modest, lengthscale \(\xi\) characterises the lengthscale of a ‘mosaic’ comprised of distinct aperiodic solutions of the free energy functional. The domain walls separating the mosaic cells are relatively strained regions that give rise to qualitatively new physics that are not directly accessible to meanfield approximations. In particular, vibrational excitations of the domain walls quantitatively account for the phenomena associated with the Boson peak and the thermal conductivity plateau. In amorphous semiconductors characterised by spatial variation of bond saturation, the domain walls are also predicted to host special, very deep midgap electronic states which are revealed by exposing a pristine sample to macroscopic amounts of photons at near gap frequencies.

The non-meanfield nature of the RFOT-based calculation is key to one’s ability to capture physics associated with reconfigurations on finite timescales. The finiteness of the cooperativity length \(\xi\) is directly linked with the finiteness of the relaxation barrier in a liquid near the glass transition, which is kinetically controlled. The present author believes that the mechanical stability of a glassy liquid on lengths less than \(\xi\) can be thought of as the bare degrees of freedom from the Yu–Leggett infinite-range scenario largely frozen out on all length scales less than \(\xi\). As a result,
these degrees of freedom no longer contribute significantly to phonon scattering while the cooperative motions on the length $\xi$ are the only remnants of the liquid motions. The density of states of these nanoscopic regions is considerably lowered in comparison with that for the bare degrees in the infinite-range scenario due to Yu and Leggett. Indeed, the typical energy spacing is now on the order of $T_g$ implying resonant interactions between these degrees of freedom are unlikely and do not significantly affect thermal properties. The interaction still manifests itself in subtle ways already at near-Kelvin temperatures because of their multi-level nature, for instance, by causing a negative thermal expansivity. Direct determinations of the cooperativity length $\xi$, together with dozens of quantitative predictions made by the RFOT theory [31,32] – including predictions for the density of states of the excess structural degrees of freedom observed in cryogenic glasses – give confidence in this microscopic picture. Some of the most direct microscopic signatures of the non-trivial length $\xi$ in frozen glasses are the Boson peak and the topological midgap electronic states in amorphous semiconductors.

The ability of a glassy liquid to stabilise or age via cooperative reconﬁgurations may be also key for assessing the relatively recent proposal for the low-$T$ glassy anomalies as stemming from marginal stability on the approach to Gardner instabilities predicted to take place in meanﬁeld liquids. In the latter picture, discussed in Section 4, the liquid is unable to reconfigure below the temperature $T_A$ at which metastable structures begin to form and can be thought of as residing all in the very same aperiodic free energy minimum. This is because interconversions between the minima are subject to strictly inﬁnite barriers in the meanﬁeld limit. Yet in ﬁnite dimensions the liquid is broken up into a mosaic made of distinct aperiodic solutions, as discussed in Section 3. The cost of making the mosaic, $\gamma N^{1/2}$ per domain, is exactly compensated by the entropic stabilisation, $-Ts_N$ per domain, at the cooperative size $N^*$. Still, the mosaic is more stable than a bulk aperiodic state, at ﬁnite temperatures, because of the ﬁnite entropy of the domain walls [85]. The Gardner-unstable regions – where the free energy density is typically higher – thus can be viewed as resulting at least in part from the inability of the liquid to fully (entropically) stabilise.

Going beyond meanﬁeld theory, LW [57] have argued that quench-induced instabilities in ﬁnite dimensions would require very high kinetic pressures that are in signiﬁcant excess of those achievable in a glass using a conventional thermal quench. In fact, achieving such kinetic pressures requires ambient pressures on the order of several Gigapascales. In addition, any incipient criticality associated with the Gardner instability would be destroyed by the activated ageing events. For these reasons, the Gardner
instabilities were argued not to be the cause of the cryogenic anomalies observed in structural glasses.

On the question of scale invariance or absence thereof in the context of the emergence of rigidity in structural glasses, one may legitimately enquire as to the current status of renormalisation group (RG)-based treatments of the glass transition. Such treatments have often been the tool of choice in testing for scale invariance. As pointed out in Ref. [156], RG calculations are particularly difficult to implement for liquid-to-solid transitions because the very nature of the degrees of freedom changes entirely at the transition, viz., from density fluctuations above $T_{cr}$ to vibrations of an essentially fixed lattice below $T_{cr}$. These difficulties can be partially circumvented in glasses [33] by using a related spin model that happens to exhibit, in the mean field limit, the dynamical transition analogous to the crossover and even the putative Kauzmann singularity at the temperature $T_K$, Equation (36). If one could equilibrate the sample at $T_K$, the configurational entropy would vanish while the relaxation barrier would strictly diverge.

Angelini and Biroli [33] have argued, using a spin model and an approximate RG scheme that above spatial dimensions 4, one indeed should expect two zero temperature fixed points that correspond with the crossover and the Kauzmann crisis. ‘Zero temperature’ implies that the ratio of the coupling strength to temperature diverges at the transition. At finite temperatures, this corresponds with an infinitely deep bound state. Such bound states are characteristic of asymptotically free theories [157, 158]. In the context of solids, such infinitely deep bound states are natural: To break a single bond, an infinitely many bonds must be broken. Incidentally, Bevzenko and Lubchenko [37, 38] have shown at the Onsager-cavity level that elasticity is, in fact, an asymptotically free theory. For dimensions 4 and below, however, those fixed points are avoided [33]. In 3D, the correlation length reaches a value numerically close to 15, instead of diverging. In view of Equation (34), even such a modest size implies super-cosmological relaxations times [156], thus making it impossible to observe avoided criticality in conventional glass-formers. We must also note that even if the Kauzmann state does in principle exist in 3D – extrapolations of the configurational entropy suggest that it does! – detailed calculations still indicate that the Kauzmann state would be avoided in 3D owing to nano-crystallisation or a similar type of local ordering [159].

One of the challenges posed by the cryogenic anomalies in glasses is that direct probes of the spatial extent of the structural resonances have not been found in the laboratory. We reiterate that there are, in principle, three relatively distinct options for the resonance size: One is that these puzzling degrees of freedom involve motions of at most a few
particles, as in the original TLS proposal [3,4] or its soft-potential
generalisations [13–15]. Another size follows from the RFOT theory,
which dictates that while the resonances are still local – and quite
compact! – they involve significantly more atoms, several hundreds or
so, and thus each span a region a few nanometers across. Finally in
infinite-range scenarios à la Yu and Leggett, the resonance could be
formed by two primitive degrees of freedom that could be separated by
an arbitrarily large distance. Since even such arbitrarily extended degrees
of freedom can absorb/emit phonons resonantly at the low energies in
question, existing experiments that probe defect states, such as phonon
echo [16] or spectral diffusion [120,160,161], do not probe the spatial
extent of those defects. The situation is even worse when the chromo-
phore is coupled to the structural resonances electromagnetically since
for the same amount of exchanged energy, the wavelength of light is
much greater than that for sound. Incidentally, the apparent dipole
moment for structural rearrangements is relatively large, on the order
of a Debye [18]. Within the RFOT-based framework [30,78], such a
large dipole moment comes about through a cumulative effect of a large
number of small elemental dipole moments generated by rotations of a
close pair of particles in a polar substance. Conversely, it is difficult to
imagine how such a large dipole moment would be generated by motion
of just a few particles in a very dense glass. I note in passing that the
‘electrodynamics’ of the TLSs is not limited to their exhibiting a dipole
moment. Some of the glasses show very puzzling magnetic-field effects
[162], discussion of which is beyond the scope of this article; a recent
review is available in Ref [163]. It appears that these magnetic field
effects are consistent with the multi-particle picture advanced by the
RFOT theory.

To address some of the challenges faced by existing spectral diffusion
setups, in which one looks at a single chromophore at a time, Lubchenko
and Silbey proposed [164] that such setups can be modified to separately
determine the concentration of the resonances and their coupling to the
phonons (or photons). In this modified setup, one employs not one but
two or more chromophores and monitors simultaneously the evolution of
their frequencies. The idea behind such ‘molecular binoculars’ is that high-
frequency, low-magnitude spectral jumps of the chromophores are due to
remote defects. Such jumps will be correlated even for relatively well-
separated chromophores because their respective sets of remote defects
mutually overlap. In contrast, large-magnitude rare jumps will sense only
those defects found in the immediate vicinity and thus will be uncorre-
lated. Thus, according to Ref. [164], two chromophores placed at a dis-
tance $r \approx 200$ nm, at a temperature near 0.1 K, will decorrelate after about
one tenth of a millisecond. The two-chromophore setup allows one to
separate out the concentration of the defects because it introduces an additional lengthscale in the problem, viz., the distance between the chromophores. It would be interesting to investigate whether such a setup could be used to differentiate between the local and Yu-Leggett scenarios. Presumably, the non-local nature of the compounds resonances implies the spectral jumps of two remote chromophores will be correlated even on relatively long time scales.

An entirely distinct avenue for tests of the molecular motions underlying the cryogenic degrees of freedom is afforded by the amorphous chalcogenides or any other materials that could host the topological midgap electronic states. Just as in the context of conjugated organic polymers \[122\], ENDOR experiments have been proposed as a way to detect the mobile subset of structural resonances \[35\]. In addition, positron-annihilation lifetime spectroscopy (PALS) is a very sensitive probe of defected configurations in glasses. Note that the traditional interpretation of PALS as a tool to probe ‘micro-cavities’ does not seem to work well in the chalcogenides \[165\]. One the other hand, positrons would definitely interact with the midgap states, which, recall, are \textit{charged} in pristine samples; it is hoped that these experiments will eventually enable one to determine the absolute, not just relative concentration of positron scatterers. If directly confirmed, the association between the structural resonances and the midgap electronic states would indeed provide direct, strong support for the RFOT-advanced, local scenario: In contrast with the massless phonons, the wavefunction of an electron can extend, within a mobility gap, by at most few nanometers. Based on this notion and many other quantitative predictions of the RFOT theory \[31,32\], the present author is convinced the physics underlying the cryogenic anomalies is largely local but not single-particle; the extended structural degrees of freedom are frozen out already above the glass transition.

Last but not least, there has been recently a surge of interest in low-temperature anomalies in disordered films. In fact, TLS-like excitations are deemed to be a key contributor to the loss of coherence in Josephson junctions, which are an important candidate system for quantum computing \[44–47,166\]. It is hoped that this contemporary and fascinating application will revive interest in what many – though not the present author! – would consider quite literally a cold case of the contested relics of the liquid motions exhibited by cryogenic disordered solids.

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Disclosure statement

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