

The frustration-based approach of supercooled liquids and the glass transition: a review and critical assessment

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TOPICAL REVIEW

The frustration-based approach of supercooled liquids and the glass transition: a review and critical assessment

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Received 2 August 2005

Published 2 December 2005

Online at stacks.iop.org/JPhysCM/17/R1143

Abstract

One of the most spectacular phenomena in physics in terms of dynamical range is the glass transition and the associated slowing down of flow and relaxation with decreasing temperature. That it occurs in many different liquids seems to call for a ‘universal’ theory. In this article, we review one such theoretical approach, which is based on the concept of ‘frustration’. Frustration in this context describes an incompatibility between extension of the locally preferred order in a liquid and tiling of the whole space. We provide a critical assessment of what has been achieved within this approach and we discuss its relation with other theories of the glass transition.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

One of the disappointing aspects of the study of the glass transition is that after many years of scholarly effort there remains wide divergence in the basic ways in which relevant phenomena are envisaged. By ‘basic ways to envisage phenomena’ we mean the physical models upon which relevant theories of structure and dynamics can be built, i.e., the zeroth-order descriptions which with but minor elaboration should enable one to describe universal or species-independent phenomena over a wide range of control variables such as temperature and pressure. Perhaps such great differences of viewpoints exist because no such zeroth-order description can be constructed, but we do not believe this to be the case. What might be described as the ‘anomalous slowing down’ of relaxation and flow in liquids with the approach to the glass transition appears to be a sufficiently general phenomenon to be describable by a ‘universal’ theory.

We review in this article one such theoretical approach which has been developed over the past two decades: it is based on the idea that the physical mechanism which is responsible for glass formation is the ubiquitous presence of ‘*frustration*’ in liquids. ‘Frustration’ in this context describes an incompatibility between extension of the local order preferred in a liquid and tiling of the whole space.

After briefly summarizing the phenomenology of glass-forming liquids in light of what we think to be the relevant physics (section 2), we introduce the concept of frustration. We first describe what is probably the most studied example, that of frustrated icosahedral order in metallic glass-formers, and we summarize the curved-space approach of geometric frustration (section 3). In section 4, we discuss the statistical mechanical description of frustration in liquids, with both the underlying assumptions and the possible candidates for providing a minimal theoretical model at a coarse-grained, mesoscopic level. We next present the evidence and the consequences of a generic property shared by the frustrated models for the glass transition, that of ‘avoided criticality’ (section 5). In section 6, we review a phenomenological scaling approach to supercooled liquids built about an avoided critical point, the frustration-limited domain theory, and in section 7 we summarize the results of extensive computer simulation studies of three-dimensional Coulomb frustrated lattice models. The following section is devoted to discussing additional phenomena brought about by frustration, the emergence of a complex free-energy landscape characterized by a proliferation of long-lived metastable states and the presence of topological excitations (defects) whose effective dynamics may be strongly constrained; this allows us to make contact with other theoretical approaches of glass formation (section 8). Finally, section 9 presents some concluding remarks.

This article is intended to provide a critical assessment of what has been achieved within the frustration-based approach of glass-forming liquids, discussing the limitations and the open questions.

2. Phenomenology: what is there to be explained?

What is meant by the ‘glass transition’ is not always well specified, but usually it refers to the passage from liquid-like behaviour to behaviour characteristic of amorphous solids. The ‘glass transition’ so defined is not a thermodynamic, nor even a dynamic, transition; it is a point of dynamic arrest arbitrarily but narrowly specified by the available experimental techniques for studying flow or relaxation. We focus here on the approach to this glass transition, when the liquid or the polymer can still be considered at equilibrium (although it may be ‘supercooled’ and therefore in metastable equilibrium, the most stable phase being a crystal).

The distinctive property of glass-forming liquids and polymers is the dramatic slowing down of relaxation and flow with decreasing temperature [1–3]. The dynamical range of this phenomenon is probably one of the most spectacular in physics: viscosity and main (α) relaxation time may increase by some 15 orders of magnitude for a mere 30% decrease in temperature. Especially striking is the fact that for most liquids (notable exceptions are network forming systems with strong directional bonding such as silica glasses) the slowing down occurs much more rapidly than one would have anticipated by extrapolating the behaviour of the ‘ordinary’ liquid, say above its melting temperature T_m . For instance, extrapolation of the high-temperature data for the viscosity of liquid *ortho*-terphenyl, which are well described by a simple Arrhenius dependence, $\eta \approx \eta_\infty \exp[E_\infty/(k_B T)]$, would imply a glass transition temperature (conventionally defined as the point at which the viscosity takes a given value of 10^{13} Poise) at very low temperature some 150–200 K below the actual $T_g \approx 243$ K: see figure 1. This points towards the existence of a crossover temperature T^* below which the dynamical properties of a liquid change from an ‘ordinary’, Arrhenius-like temperature dependence to an ‘anomalous’, stronger than Arrhenius (or super-Arrhenius), one. Such an anomalous dependence, which is observed in all kinds of liquids and polymers irrespective of their detailed molecular properties [1–3], suggests a collective phenomenon involving cooperative motion of a large number of molecules.

The notion of ‘fragility’, introduced by Angell to classify glass-forming liquids and polymers [5], characterizes the degree of super-Arrhenius behaviour; the more fragile the glass-former the greater the super-Arrhenius character. The strong temperature dependence of the viscosity and α -relaxation time of glass-forming liquids is often described by a Vogel–Fulcher–Tammann formula, $\eta \approx \eta_\infty \exp[DT_0/(T - T_0)]$, D being a measure of fragility. This description implies the presence of a dynamical singularity at a temperature T_0 lower than T_g . (However, T_0 is always found quite far below T_g : at least 40 K for the fragile liquid *ortho*-terphenyl, see figure 1.) An alternative way of representing the data is to focus on the effective activation (free) energy, $E(T) = k_B T \ln(\eta/\eta_\infty)$. In this representation, the crossover behaviour shows up quite clearly, as illustrated in figure 2 for several liquids.

Another characteristic of the approach to the glass transition, which becomes more manifest in the temperature range below the crossover discussed above, is the spatially ‘heterogeneous’ nature of the relaxation. The most easily detected, yet not uniquely interpretable, signature of such heterogeneity is a stretching of the relaxation functions, i.e., a deviation from simple exponential dependence at long times (or the equivalent broadening in frequency space for the dynamic susceptibilities); this is often represented by a stretched exponential in time, $\phi(t) \sim \exp(-(t/\tau_\alpha)^\beta)$, where τ_α is the α -relaxation time. More direct experimental evidence for the presence of supermolecular dynamically correlated regions in

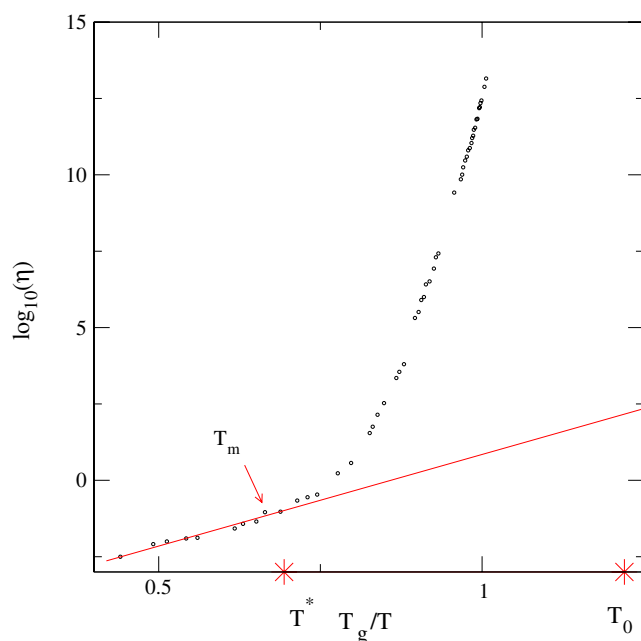


Figure 1. Super-Arrhenius temperature dependence of the viscosity of liquid *ortho*-terphenyl: logarithm (base 10) of η versus inverse temperature T_g/T . The straight line is the extrapolation of the behaviour in the 'ordinary' liquid range (above T_m); whereas the actual T_g is around 243 K, the extrapolated one is at a much lower temperature around 50–70 K. T^* and T_0 are the temperatures of the apparent crossover from Arrhenius to super-Arrhenius behaviour and of the extrapolated divergence of the viscosity, respectively. (Data taken from references cited in [4].)

supercooled liquids has been provided in the past ten years (see the reviews [7–9]). This, too, suggests collective behaviour; however, the measured (linear) size of the correlated regions never exceeds 5–10 molecular diameters at T_g [10].

An additional puzzling feature of the glass transition problem is that the spectacular change in the dynamical properties does not come with a related growth in thermodynamic correlations [1–3]. No convincing evidence has been so far reported for a significant increase in structural correlations: the evolution of the static pair structure factor appears weak and featureless even in very fragile glass-formers. The only noticeable observation is the decrease of the excess entropy, defined as the difference between the entropy of a supercooled liquid and that of the associated crystal, with decreasing temperature [11]. This decrease appears correlated with the slowing down of the relaxation, being larger for more fragile glass-formers [10].

We can then summarize our view of the phenomenology of supercooled liquids as follows: glass formation seems to be a *collective or cooperative* (we use the two terms interchangeably) phenomenon, which would account for the rather universal trends observed in many different systems, but cooperativity occurs on a *limited, mesoscopic spatial scale*.

As we mentioned in the introduction, the absence of a unique reading of the salient aspects of the phenomenology of glass-forming liquids goes with the absence of a widely accepted theory of the glass transition. There is indeed a variety of theoretical approaches, which often appear at odds with one another. The one feature that most theories have in common, though, is the idea that the slowing down of relaxation and flow in supercooled liquids (especially in the fragile ones) is spectacular enough and general enough to be describable by a universal

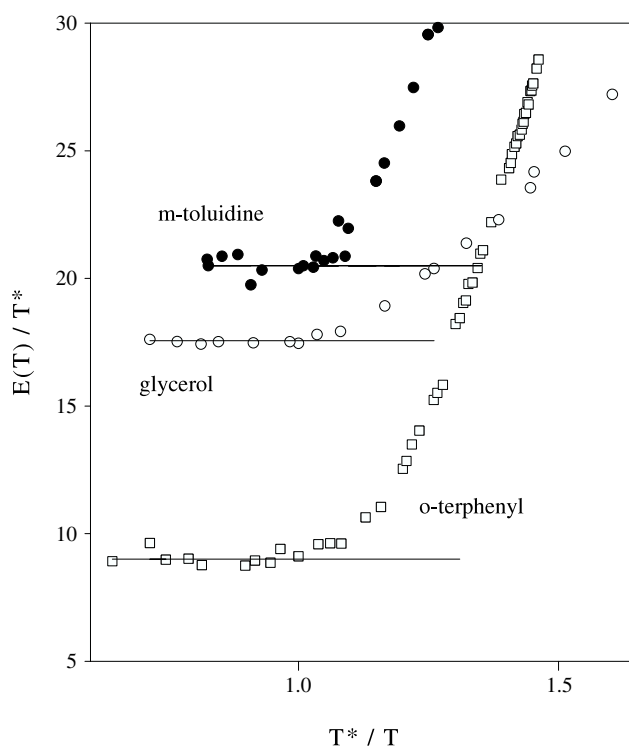


Figure 2. Crossover from Arrhenius to super-Arrhenius behaviour for several glass-forming liquids: effective activation (free) energy $E(T)$ versus $1/T$. Both $E(T)$ and T are divided by the crossover temperature T^* . (Data taken from references cited in [4] and [6].)

theory and that, as is quite natural in physics, universality is associated with the presence of one or several underlying critical points: the putative critical points may be dynamic [12–15] or thermodynamic [16–22], but, as no divergences or singularities are actually observed, these critical points are postulated to be either unreachable [16–19, 14, 15, 21, 22], i.e., occurring below the experimental T_g , or avoided [12, 20], being only present in an ideal system ‘near’ to the real liquid (see figure 3).

In this article, we review one such theoretical approach, which is based on the concept of *frustration*. Frustration, meant here to describe an incompatibility between the locally preferred order in a liquid and the global requirements for tiling of space, is an appealing candidate for generating collective (cooperative) behaviour on a limited spatial scale and bringing in static spatial correlations only at a multi-particle level that cannot be probed by usual experimental techniques.

3. Geometric frustration in simple atomic systems: the curved-space approach

The concept of frustration was introduced by Toulouse in 1977 [23] in the context of spin models to describe situations in which one cannot minimize the energy of the system by merely minimizing all local interactions. A simple illustration is provided by an Ising spin model on a triangular lattice with antiferromagnetic interactions between nearest-neighbour spins: an elementary ‘plaquette’ of the lattice made by one triangle of nearest-neighbour sites

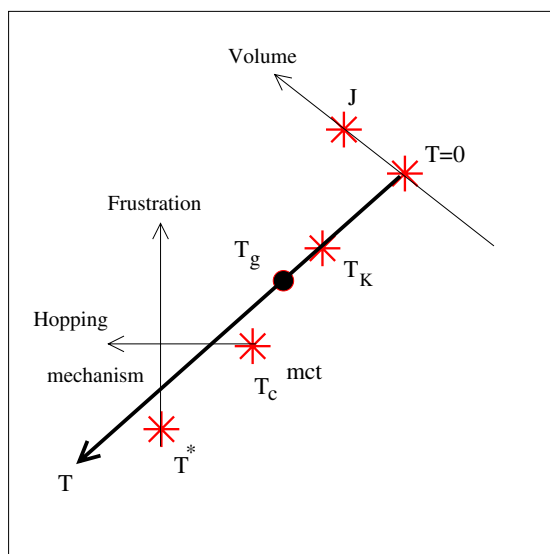


Figure 3. Schematic representation of (critical) theories of the glass transition in a virtual multidimensional diagram: the physical axes (temperature, volume) are complemented by abstract dimensions (frustration, hopping mechanisms). Avoided critical points: $T^* = T_c^{(0)}$, critical point in zero frustration; T_c^{MCT} , dynamic singularity of mode coupling theory. Unreachable critical points below T_g : T_K , entropy crisis or random first-order critical point; $T = 0$, dynamic critical point for kinetically constrained models; point J , jamming transition. (See text for references.)

is frustrated because the three antiferromagnetic interactions along the bonds forming the plaquette can never be satisfied simultaneously (see figure 4). Spin glasses are a well known example of frustrated systems; however, in this case frustration is induced by the presence of quenched disorder, due for instance to frozen-in impurities [24]. This inhomogeneous and externally imposed frustration is not relevant for supercooled liquids in which glassiness and heterogeneous behaviour are self-generated. To emphasize the difference, frustration in the context of liquids has been given several qualifying adjectives, such as ‘uniform’, ‘geometric’, ‘topological’, or ‘structural’. In what follows however we shall simply refer in most cases to ‘frustration’ without adding any epithet.

What has often been taken as the paradigm of (geometric) frustration in amorphous systems is the case of icosahedral order in simple one-component liquids in which the atoms interact through spherically symmetric pair potentials. The ground state of four atoms is a perfect tetrahedron, with the atoms sitting at the vertices, and 20 such tetrahedra can be combined to form a regular 13-atom icosahedron (figure 5). Frank [25] was the first to stress the importance of local icosahedral order in simple atomic liquids and liquid metals. He showed that the most stable cluster made of a central atom and a shell of 12 neighbours is indeed an icosahedron, and not an arrangement associated with the actual crystalline phases, bcc, fcc, or hcp. In three-dimensional Euclidean space, however, this locally preferred structure (tetrahedral or icosahedral) cannot propagate freely to tile the whole space: this is what is meant by *geometric frustration*. The global ground state of the system is instead an fcc or hcp crystal.

The concept of frustration is more easily grasped by contrasting the case of spherical particles in three dimensions with other situations [26, 27]. Systems of spherical particles in two-dimensional Euclidean space, i.e. discs on a plane, are not subject to frustration: the locally preferred structure is a regular hexagon, with one atom at the centre and six neighbours at the

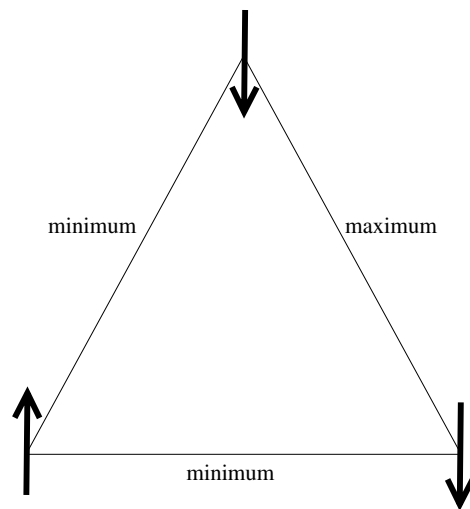


Figure 4. Elementary plaquette of a triangular lattice. When interactions between nearest neighbour Ising spins are antiferromagnetic, one can never satisfy (i.e. anti-align spins) more than two bonds at the same time.

vertices, and this structure can be periodically repeated to form a triangular lattice. Similarly, aligned hard cubes in three-dimensional Euclidean space form simple cubic arrangements that are both locally and globally preferred, therefore excluding any frustration effect [28].

As illustrated in figure 5, frustration can be envisaged from various different angles: as a global constraint, e.g., the incompatibility between the fivefold rotational symmetry of the icosahedron and translational periodicity (figure 5(a)), or, more in line with the usual definition of frustration (see above), as the impossibility to let all the atoms simultaneously sit in positions corresponding to the minima of the pair potentials between nearest neighbours (figure 5(b)).

An important observation is that frustration can be turned off by ‘curving’ space [29, 27]. One can play with the metrics and topology of the underlying space in order to let the local order propagate freely and generate a regular tiling or ‘tessellation’. This can be understood for instance by considering figures 5(b) and (c): if space can be curved so that the defect angle made by five tetrahedra packed along a bond as well as the mismatch between the two interatomic distances d and a in an icosahedron vanish, propagation of tetrahedral/icosahedral order becomes possible. Indeed, a perfect icosahedral phase can be formed on the surface S^3 of a four-dimensional hypersphere with a radius tuned to be $5/\pi = 1.5915\dots$ times the preferred interatomic geodesic distance (in curved space). This ideal icosahedral structure is called the polytope $\{3, 3, 5\}$ [27, 30].

The core of the curved-space approach of amorphous (liquid and glassy) phases, developed on one hand by Sadoc, Kleman, and Mosseri [29, 27, 31–33] and on the other by Nelson and co-workers [34, 35, 26, 36–38] and Sethna [39, 40], consists in using this ideal structure as a reference state (for reviews see [26, 27, 41, 42]). Going back from the reference state to the actual configurations in ‘flat’ (Euclidean) space necessarily forces in topological defects that perturb the ideal order. All sorts of defects can be generated, but it was argued that the most relevant for the physics of atomic glasses are ‘disclinations’ [32, 27, 34, 35]: disclinations are associated with the breaking of rotational, here bond-orientational, symmetry (their counterpart for translational symmetry is the ‘dislocations’), and they are line defects in three dimensions [43]. Such topological defects are expected to form a disordered network,

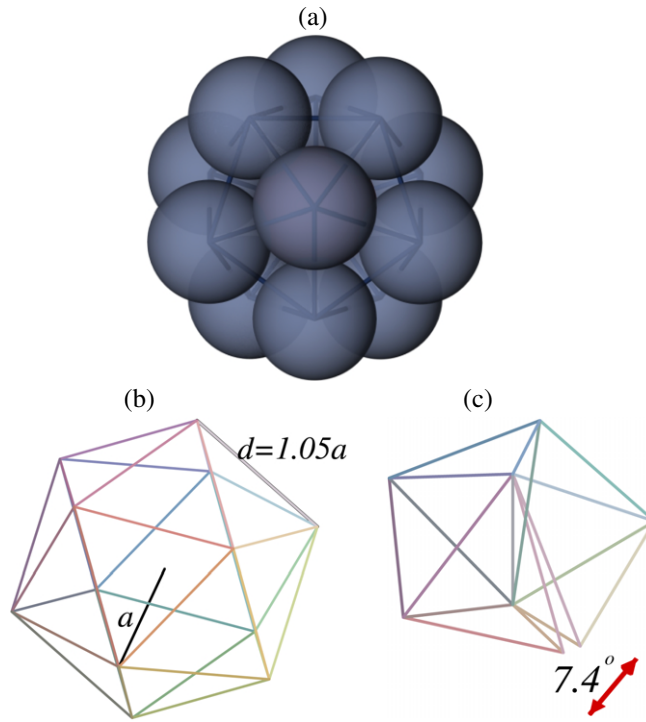


Figure 5. Manifestations of frustration for tetrahedral/icosahedral order in 3D atomic systems: (a) the fivefold rotational symmetry of the icosahedron shown here is not compatible with translational periodicity. (b) The distance d between the atoms of the first shell is slightly larger than the distance a between the central atom and its neighbours: $d = 1.05 \cdot \cdot \cdot a$. (c) The dihedral angle of the tetrahedron, $\cos^{-1}(1/3)$, is not commensurate with 2π so that five tetrahedra packed along a bond leave a defect angle of about 7.4° .

the actual amorphous phases being composed of locally ideally ordered regions interrupted by defects⁵. Interestingly, the network of defects (disclinations) may itself become ordered at low temperature, thereby leading to ‘defect-ordered phases’ whose best examples in the case of metallic systems are the Frank–Kasper phases [27, 44, 45].

Whereas Sadoc and Mosseri focused on the most efficient way to produce dense amorphous packings by decurving the polytope $\{3, 3, 5\}$, Nelson and co-workers [36–38, 26] developed a statistical mechanical approach of frustrated icosahedral order. They built a set of local order parameters $\mathbf{Q}_\ell(\mathbf{x})$ by projecting a local particle configuration centred on position \mathbf{x} onto the surface of a tangent four-dimensional hypersphere with appropriate radius to accommodate the polytope $\{3, 3, 5\}$ and, much in the spirit of the Ginzburg–Landau theory of freezing, they derived a free-energy functional of this local order parameter [36],

$$F[\mathbf{Q}_\ell] = \int d^3x \left\{ \frac{1}{2} Z_\ell |D_\mu \mathbf{Q}_\ell(\mathbf{x})|^2 + \frac{1}{2} \tau_\ell |\mathbf{Q}_\ell(\mathbf{x})|^2 + \mathcal{O}(\mathbf{Q}_\ell^3) \right\}, \quad (1)$$

⁵ There is some flexibility in defining the disclinations in the present case. Defects are indeed always considered relative to a given, usually ordered, ground state. Here, the ground state has perfect icosahedral order but lives in a curved space. Disclinations can then either be considered relative to the ideal icosahedral template, and the geometric constraints then force an excess of disclinations of a given sign (essentially, wedge disclinations carrying a ‘charge’ of -72°) [35, 32, 27]; or they can be treated as ‘curvature carrying’ lines, constructed from some ground state living on a ‘corrugated’ space with regions of positive and negative curvature but with zero mean curvature: in this case, positive and negative disclinations must balance each other to ensure that space is ‘flat’ on average [27, 33].

where the index μ is associated with the spatial coordinates in ordinary 3D Euclidean space (e.g., $\mu = x, y, z$ for Cartesian coordinates); the local order parameter $\mathbf{Q}_\ell(\mathbf{x})$ transforms according to the representation of dimension $(\ell+1)^2$ of $SO(4)$, Z_ℓ and τ_ℓ are phenomenological parameters, and $O(\mathbf{Q}_\ell^3)$ denotes cubic and higher-order invariants built with \mathbf{Q}_ℓ . The most relevant value of ℓ for describing icosahedral order is 12, but $\ell = 20, 24, 30, 32, \dots$ are also allowed by symmetry ($\ell = 0$ corresponds to the mean particle density).

Frustration is introduced via the so-called ‘covariant derivative’ entering the gradient term. Following a suggestion made by Sethna [39, 40], it is defined by requiring that the gradient term be a minimum when two nearby local particle configurations are related by ‘rolling without slipping’ the tangent hypersphere carrying the reference icosahedral template along the path joining the configurations. This leads to [36]

$$D_\mu \mathbf{Q}_\ell(\mathbf{x}) = \partial_\mu \mathbf{Q}_\ell(\mathbf{x}) - i\kappa \hat{\mathbf{L}}_{0\mu}^{(\ell)} \mathbf{Q}_\ell(\mathbf{x}), \quad (2)$$

where the $\hat{\mathbf{L}}_{0\mu}^{(\ell)}$ denote the generators of the $SO(4)$ rotations in the $(0, \mu)$ plane (0 denotes the direction in the four-dimensional space embedding S^3 which is perpendicular to the tangent Euclidean space described by the Cartesian coordinates $\mu = x, y, z$) and κ is the inverse radius of the hypersphere S^3 compatible with the polytope {3, 3, 5}. Here and in the following, the Einstein convention is used, in which one sums over indices whenever they are repeated. The covariant derivative is frustrated because it cannot be minimized (i.e., set equal to zero) everywhere.

Despite its many appealing features, this curved-space approach of frustrated icosahedral order has led in practice to meagre results concerning the glass transition phenomenon itself. Several factors may explain this shortcoming. First, the models, such as the $SO(4)$ uniformly frustrated theory described above, are rather complex and have never been fully analysed: for instance, the topological defects have been characterized [35, 34, 36] and the static structure factor of metallic glasses has been reproduced [37, 38], but no attempts have been made to study the dynamics.

Second, difficulties may arise from the fact that local icosahedral order in simple atomic systems appears strongly frustrated. The typical distance between defects, expected to be of the order of or less than the radius of the reference hypersphere κ^{-1} , is small, one or two particle diameters at most, which precludes a separation between a mesoscopic, coarse-grained description of collective effects and a detailed account of the microscopic properties. (This may also explain the controversy about the extent of icosahedral order and associated correlations in amorphous phases composed of spherical particles.) It is worth noting that simple atomic systems are not good glass-formers and appear quite ‘non-fragile’ with an essentially Arrhenius temperature dependence of the viscosity and α -relaxation time [46]; this is also true for the Lennard-Jones models studied in computer simulations which, in spite of the weakness of the interatomic bonding, are much less fragile than typical molecular glass-forming liquids [47].

Finally, if glass formation is indeed a ‘universal’ phenomenon whose most salient properties are largely independent of molecular details (in a sense discussed in the preceding section), icosahedral order is likely to be too material specific. Possible generalizations to describe frustration in liquids are reviewed in the next section.

4. Statistical mechanics of frustration in liquids

Application of the concept of frustration to liquids boils down to three propositions which are plausible and, as discussed above, reasonably well established in the case of systems of spherically symmetric particles, but still remain at the level of postulates in the case of molecular liquids, mixtures, and polymers. These propositions can be summarized as follows.

(1) *A liquid is characterized by a locally preferred structure (LPS) which is different than that of the crystalline phases.* This LPS is an arrangement of molecules that minimizes some local free energy (an operational definition of such a local free energy is given in [48]), much in the same way as the local tetrahedral/icosahedral order in liquids of spherical particles. Description of such an LPS requires the knowledge of multi-particle densities, beyond the usual one-body density, and of multi-particle correlations, beyond the usual pair correlations. For instance, even in simple atomic liquids, information on local bond-orientational order involves at least two-body densities and four-body correlations [49–51]. For this reason, the signature of an LPS is hard to detect in common diffraction experiments in which one has only access to the (pair) structure factor of a liquid or a glass.

The LPS may change at high enough pressure: this is the case, for instance, of water and tetrahedrally bonded liquids for which the low-pressure LPS that tends to minimize the local energy by satisfying the maximum number of directional (hydrogen- or covalent) bonds goes over to a different structure at high pressure, where packing effects dominate over bonding effects [52–54]. However, at a given pressure or density, the LPS does not change with temperature; it just becomes more and more favoured as temperature decreases.

(2) *The LPS characteristic of a given liquid cannot tile the whole space.* This incompatibility between local order and global space filling is precisely the content of the concept of *frustration*. Were it not for frustration, the LPS could propagate through the whole space and form an ‘ideal’ ordered phase that would supersede the actual crystalline phases. Instead of this, the actual crystal is formed via a strong first-order transition that requires a rearrangement of the local structures, a cost that is more than compensated by the free-energy gain due to the global tiling of space. So, as suggested by Frank [25], the presence of frustration is the possible physical ingredient allowing supercooling of a liquid at temperatures below the melting point.

(3) *It is possible to construct an abstract reference system in which the effect of frustration is turned off.* At a microscopic level, frustration implies that the atoms or the molecules cannot simultaneously sit in the minima of all pairwise interactions with their nearest neighbours. By allowing one to modify the topology and the metrics of the underlying space, one can get rid of frustration. This is the essence of the curved-space approach of icosahedral order (see above). In an abstract parameter space, one can now think of frustration as a tunable control variable. However, a given liquid is of course characterized by a given level of frustration, a given LPS, and a given reference space.

Note also that in the absence of frustration ‘ideal’ ordering is likely to proceed via a continuous or weakly first-order transition, quite differently from the standard melting in 3D flat space. For instance, the melting transition of parallel cubes, a system with no frustration between local order and global tiling in ordinary 3D space, has been shown to be continuous [28]. Similarly, Nelson and his co-workers [36–38, 26] have argued that bond-orientational ordering is likely to occur via a continuous or weakly first-order transition in three dimensions, even in the presence of cubic invariants in the Landau description of the system [55, 50]. (Icosahedral ordering in the polytope $\{3, 3, 5\}$ on S^3 [56] does not occur by a true phase transition at all since the underlying space is the surface of a 4D sphere of finite radius.)

The next step is to build a statistical mechanical description of glass-forming liquids based on the above propositions. We will take here the point of view that if indeed, as argued in discussing the phenomenology, the viscous slowing down of supercooled liquids and the resulting glass transition are universal, progress can be made by relying on a coarse-grained, mesoscopic approach that incorporates the effect of frustration while, at least in a first step,

overlooking a detailed description of the LPS, of the reference space, and of the precise mechanism by which frustration operates⁶.

A *minimal theoretical model* of frustration in glass-forming liquids should satisfy, on top of the overall consistency with the physical picture developed above, some prerequisite properties, such as (i) frustration should be a tunable parameter, which allows one to investigate the potential connection between frustration and ‘fragility’ in glass-formers, and (ii) frustration should be uniform, i.e., the same at every point of space and, consequently, not due to the presence of quenched disorder. We review below some of the paths that have been, and still are, followed. (Note that in all these descriptions the actual crystal is excluded from the picture, in order to focus on the liquid and supercooled liquid phases.)

4.1. Coupling to a non-Abelian gauge background

The statistical mechanical treatment of icosahedral order put forward by Nelson and his co-workers (see above) can be extended by ignoring the precise reference of the local order parameter (and of the LPS) to the ideal tiling of the polytope $\{3, 3, 5\}$ and that of the frustration strength to the radius of curvature of the hypersphere S^3 compatible with this ideal tiling.

In a continuum, field-theoretical description, the generic form of the free-energy functional reads [57]

$$F[\mathbf{Q}] = \int d^3x \left\{ \frac{1}{2} Z |D_\mu \mathbf{Q}(\mathbf{x})|^2 + \frac{1}{2} \tau |\mathbf{Q}(\mathbf{x})|^2 + O(\mathbf{Q}^3) \right\}, \quad (3)$$

where the index μ is associated with the spatial coordinates in ordinary 3D Euclidean space; the local order parameter $\mathbf{Q}(\mathbf{x})$ transforms according to the representation of dimension n of a given non-Abelian continuous Lie group, Z and τ are phenomenological parameters, and $O(\mathbf{Q}^3)$ denotes cubic and higher-order invariants built with \mathbf{Q} .

The ‘covariant derivative’ entering the gradient term is defined as

$$D_\mu \mathbf{Q}(\mathbf{x}) = \partial_\mu \mathbf{Q}(\mathbf{x}) - ig A_\mu^\alpha \hat{\mathbf{L}}_\alpha \mathbf{Q}(\mathbf{x}), \quad (4)$$

where the $\hat{\mathbf{L}}_\alpha$ denote the generators of the representation of dimension n of the considered non-Abelian group. The A_μ^α are coefficients depending on both ‘spatial’ indices μ and ‘internal’ indices α ; they are independent of position and play the role of a frozen, uniform gauge field (see below); the coupling strength g characterizes the magnitude of the frustration. (We recall that the Einstein convention is used for summing indices.)

The thermodynamic and structural properties of the system can be obtained from the partition function

$$\mathcal{Z} = \int \mathcal{D}\mathbf{Q} \exp[-\beta F[\mathbf{Q}]], \quad (5)$$

where $\beta = 1/(k_B T)$, whereas studying the relaxation properties requires the introduction of some local dynamical rules that reflect, at a coarse-grained level, the underlying motion of the atoms or molecules.

For example, in the theory developed by Nelson and summarized in section 3, the non-Abelian group is $SO(4)$, the main local order parameter transforms according to the representation of $SO(4)$ associated with angular momentum $l = 12$, i.e., of dimension $n = (l + 1)^2 = 169$, α denotes the six rotation planes in 4D space, $(0, x)$, $(0, y)$, $(0, z)$, (x, y) , (x, z) , (y, z) ; A_μ^α is equal to one when α corresponds to the planes

⁶ Stated otherwise, one has first to look for a minimal theoretical model which could play a role similar to the Edwards–Anderson model for the description of spin glasses [140]. The situation however is far from being as well founded as in the case of spin glasses for which the known key ingredients, quenched disorder and frustration, are appropriately accounted for by the Edwards–Anderson model.

$(0, \mu)$ with $\mu = x, y, z$ and zero otherwise, and g is equal to κ_* , the inverse of the radius of the ‘ideal’ reference hypersphere. A related, but somewhat simpler, approach due to Sethna [39, 40] corresponds to the $l = 1$ (i.e., $n = 4$) representation of $SO(4)$ (see also [57]). Lattice versions of the above free-energy functional have also been proposed [58, 57], which could make possible computer simulation studies of such theories.

In the present description, frustration is embodied in the specific form of the covariant derivative. When the coupling strength g is set to zero, the reference, unfrustrated model is chosen such that there is a continuous or weakly first-order transition to a symmetry-broken phase in which the order parameter takes a non-zero value (this phase describes the ideal order formed by extending the LPS to the whole space). When g is different from zero, frustration arises from the fact that the covariant derivative cannot be made zero everywhere. For instance, if one builds configurations by forcing the covariant derivative to vanish along straight lines starting in all directions from a given position \mathbf{x} , one finds that the covariant derivative differs from zero along any closed circuit encircling \mathbf{x} ; this leads to a large free-energy cost associated with a non-zero gradient term. (Actually, as discussed in more detail below, this cost grows super-extensively with the linear size of the region around the arbitrary chosen point \mathbf{x} , up to some intrinsic frustration length set up by the value of g .)

In the framework of differential geometry [59, 27, 43, 42], making the covariant derivative vanish along a curve amounts to parallel transporting the local order parameter (which is a vector or a tensor) along this curve. In the curved-space approach of Sethna and Nelson, this is done by ‘rolling’ a tangent 4D sphere S^3 with the ideal icosahedral template along the chosen curve in Euclidean space. Frustration then means that one cannot extend such a parallel transport to the whole space. The reason is that the covariant derivative has a non-zero curvature; this curvature is directly related to the magnitude of the difference between the initial and final values of the local order parameter after parallel transport along a closed circuit. The presence of a non-zero curvature (not to be confused with the curvature of the physical Euclidean space, which is of course zero: in the Sethna–Nelson picture, the non-zero curvature of the covariant derivative is precisely equal to that of the reference 4D sphere) comes from the non-commutativity of the generators \hat{L}_α , i.e., from the non-Abelian property of the gauge background.

An important consequence of frustration is the necessary presence of defects: the ideal order that forms the ground state of the unfrustrated system ($g = 0$) can no longer propagate freely through the whole space, and low-temperature configurations must contain an irreducible density of defects (e.g., disclination and dislocation lines, grain boundaries, etc). Such ‘topological’ defects can be studied by means of the homotopy theory [60], as done by Nelson and Widom [36] for their $SO(4)$ theory of local icosahedral order.

For completeness, it is worth interpreting the above class of models in the language of gauge field theory [43, 42]. The local order parameter $\mathbf{Q}(\mathbf{x})$ represents the matter field that is ‘minimally coupled’ to the non-Abelian gauge field. In the present case, the gauge field is frozen and uniform (hence the term ‘gauge background’ used to describe such a theory). The associated physical field, defined as the so-called covariant curl $F_{\mu\nu} = -i[D_\mu, D_\nu]$, is then given by $F_{\mu\nu} = ig^2 A_\mu^\alpha A_\nu^\beta [\hat{L}_\alpha, \hat{L}_\beta]$. It is non-zero because of the non-commutativity property of the \hat{L}_α associated with the non-Abelian nature of the ‘gauge group’ under consideration. Contact can be made with the formalism of differential geometry and tensor calculus by noticing that $F_{\mu\nu}$ identifies with the curvature tensor [43]. Note that the present theory is only globally invariant under transformations of this group. If necessary, a full blown gauge field theory in which local invariance is now enforced via a fluctuating, space-dependent gauge field could be developed; attempts in this direction have been made [61–64].

4.2. Uniformly frustrated spin models

In developing their approach based on geometric frustration for simple liquids and glasses, Nelson and his co-workers [35, 26, 38] proposed an analogy with the effect of an applied, uniform magnetic field in extreme type-II superconductors [65]. In such systems, there is always at least partial penetration of the magnetic field, no matter how small the field: this latter induces an irreducible density of defects (flux lines or vortices) of the same ‘sign’. The ground state is then an Abrikosov lattice in which those vortices form a periodic array, in a similar way as Frank–Kasper phases in which disclination lines form a periodic network are the expected ground states of simple metallic systems. The curvature mismatch that generates frustration in the curved-space approach is replaced here by the applied magnetic field.

The analogy can be made somewhat more precise in two dimensions. As discussed in section 3, there is no frustration in that case for liquids formed by one-component particles interacting via spherically symmetric pair potentials: the hexagonal LPS can propagate through the whole space to form a triangular lattice and the freezing transition is either weakly first order or splits into two continuous transitions separated by an intermediate hexatic phase characterized by bond-orientational order but no translational order. Geometric frustration can now be introduced by curving space, i.e., by placing the liquid on a hyperbolic plane H^2 , a surface of constant negative curvature $-\kappa^2$ [26, 66, 35]. Let us focus on bond-orientational order. Frustration then comes from the fact that if one measures the bond angle formed by the vector joining two neighbouring atoms with respect to a reference axis, this reference axis changes when it is parallel transported on the curved surface. (On a curved manifold, there is no global notion of parallelism, so that comparison of reference frames at different points in space requires a rule for parallel transport of vectors along curves.) A non-zero curvature implies that the reference axis does not go back to its original value when transported along any closed circuit. In the long-wavelength, continuum approach (also called ‘hydrodynamic’ in this context), the Ginzburg–Landau free-energy functional describing local hexatic order on a hyperbolic plane can be written as a modified gradient term [35],

$$F[\mathbf{n}] = \frac{1}{2} Z_H \int d^2x \sqrt{g(\mathbf{x})} |D_\mu n^v(\mathbf{x})|^2, \quad (6)$$

where $\mathbf{n}(\mathbf{x})$ is a unit vector tangent to a ‘bond’ centred at point \mathbf{x} , $g(\mathbf{x})$ is the determinant of the metric tensor $g_{\mu\nu}(\mathbf{x})$ that is appropriate for the coordinate system chosen for the hyperbolic plane, Z_H is a phenomenological hexatic stiffness constant, and the covariant derivative is given by

$$D_\mu n^v(\mathbf{x}) = \partial_\mu n^v(\mathbf{x}) + \Gamma_{\lambda\mu}^v(\mathbf{x}) n^\lambda(\mathbf{x}), \quad (7)$$

where the $\Gamma_{\lambda\mu}^v$ are the so-called connection components that define parallel transport on H^2 ; here they are simply the Christoffel symbols obtained from derivatives of the metric tensor and associated with the Levi-Civita connection. In a local Cartesian coordinate system centred at an (arbitrary) origin, one has $g_{\mu\nu}(\mathbf{x}) = \delta_{\mu\nu} - \kappa^2 x_\mu x_\nu + O(\kappa^4 x^4)$ and $\Gamma_{\lambda\mu}^v(\mathbf{x}) = \Gamma_{\mu\lambda}^v(\mathbf{x}) = -\kappa^2 \delta_{\lambda\mu} x^v + O(\kappa^4 x^3)$ for distances much less than the frustration, or curvature, scale, κ^{-1} .

Consider now the Ginzburg–Landau free-energy functional for an extreme type-II superconducting film in a perpendicular magnetic field B [65]:

$$F[\psi] = \int d^2x \left\{ \frac{\hbar^2}{2m} \left| \left(\partial_\mu - \frac{2ei}{\hbar c} A_\mu(\mathbf{x}) \right) \psi(\mathbf{x}) \right|^2 + \frac{1}{2} \tau |\psi(\mathbf{x})|^2 + O(\psi^4) \right\}, \quad (8)$$

where $\psi(\mathbf{x})$ is the complex superconducting order parameter and $\mathbf{A}(\mathbf{x})$ is the vector potential whose curl, $\partial \wedge \mathbf{A} = \mathbf{B}$, is a fixed constant (where $\mathbf{B} = B\hat{\mathbf{z}}$ is perpendicular to the plane (x, y)).

Rewriting $\psi(\mathbf{x})$ in terms of two real fields, $\psi(\mathbf{x}) = \psi^1(\mathbf{x}) + i\psi^2(\mathbf{x})$, and dropping terms other than the (modified) gradient one, equation (8) can be recast as [35]

$$F[\psi] = \frac{\hbar^2}{2m} \int d^2x |(\partial_\mu \psi^v(\mathbf{x}) + \Gamma_{\lambda\mu}^v(\mathbf{x})\psi^\lambda(\mathbf{x}))|^2, \quad (9)$$

with the ‘connection’ now defined as $\Gamma_{\lambda\mu}^v(\mathbf{x}) = (2ei/\hbar c)A_\mu(\mathbf{x})\epsilon_{\lambda v}$, $\epsilon_{\lambda v}$ being the usual antisymmetric tensor with $\epsilon_{12} = -\epsilon_{21} = 1$ and $A_\mu(\mathbf{x})$ being equal to $A_\mu(\mathbf{x}) = -(1/2)B\epsilon_{\mu\sigma}x^\sigma$, due to the uniform property of the magnetic field B (see above). Comparing equations (6), (7) with equation (9) and using the expansions of $g_{\mu\nu}(\mathbf{x})$ and $\Gamma_{\lambda\mu}^v(\mathbf{x})$ for distances less than the frustration scale, one sees a great similarity between the two systems, with B playing the role of κ^2 ; the mapping however is not exact because the tensorial content of the various objects is not quite the same (in particular the gauge group $U(1)$ associated with superconductors is Abelian, which is not the case for that associated with the connection on H^2) and because curvature introduces an intrinsic scale κ^{-1} beyond which the correspondence breaks down.

The analogy between the two kinds of systems is also striking when looking at a dual picture in terms of defects. The relevant defects in the case of hexatic ordering are disclinations, which are points in two dimensions. When frustration is weak, i.e., for small curvature, and at low temperature, it has been shown that local hexatic order on a curved surface (here, the hyperbolic plane H^2) can be described in the continuum, ‘hydrodynamic’ limit by a free-energy functional for the defect (disclination) density $s(\mathbf{x})$, [67, 68]

$$F[s] = NE_{\text{core}} + \frac{1}{2}Z \int d^2x \sqrt{g(\mathbf{x})} \int d^2y \sqrt{g(\mathbf{y})} (s(\mathbf{x}) + \kappa^2) G(\mathbf{x}, \mathbf{y}) (s(\mathbf{y}) + \kappa^2), \quad (10)$$

when the total number of defects is equal to N , E_{core} is the energy penalty associated with creating one defect, and the density of defects is defined as $s(\mathbf{x}) = (\pi/3) \sum_{i=1, \dots, N} q_i \delta(\mathbf{x} - \mathbf{x}_i)$, with $q_i = \mp 1, \mp 2, \dots$ the topological charge of the defects; $G(\mathbf{x}, \mathbf{y})$ is the inverse Laplacian on the hyperbolic plane, which goes as the Coulombic interaction $\ln(r/a_0)$, with r the distance between two defects and a_0 the core size of the defects, up to a screening length played by the intrinsic frustration or curvature scale κ^{-1} . The above expression is obtained by requiring ‘charge neutrality’, which means that $\int d^2x \sqrt{g(\mathbf{x})} (s(\mathbf{x}) + \kappa^2) = 0$ or else that the mean defect density is equal to the Gaussian curvature $-\kappa^2$ up to some trivial prefactor. This charge neutrality expresses the frustration effect of curvature that forces an irreducible density of defects of the same sign (here, point disclinations with a negative topological charge). As stated previously, this is quite similar to the frustration effect of an applied uniform magnetic field on a superconducting film, in which an irreducible density of vortices of the same sign is induced. Actually, at low temperature and in the continuum limit, the dual description of equation (8) in terms of defects leads to the following free-energy functional [69–71]:

$$F[s] = NE_{\text{core}} + \frac{1}{2}Z \int d^2x \int d^2y (s(\mathbf{x}) - f) G(\mathbf{x}, \mathbf{y}) (s(\mathbf{y}) - f), \quad (11)$$

where $G(\mathbf{x}, \mathbf{y})$ is the inverse Laplacian in flat space, i.e., goes as the Coulombic interaction $\log(|\mathbf{x} - \mathbf{y}|/a_0)$ at large distances, and $f \propto B^2$. Here too, charge neutrality imposes that the mean density of vortices is equal to f .

We have made the above rather long digression to illustrate Nelson’s analogy between glass-forming liquids and uniformly frustrated systems. Taking this analogy for granted, one may envisage as possible minimal theoretical models for glass formation simple uniformly

frustrated models⁷, either in the continuum version described above or in a lattice version, which may be more convenient for computer simulation studies. The simplest of such models is the two-dimensional uniformly frustrated XY model, whose Hamiltonian is

$$H = -J \sum_{(ij)} \cos(\theta_i - \theta_j - A_{ij}) \quad (12)$$

where the sum is over distinct pairs of nearest-neighbour sites, θ_i is the angle of the XY spin at site i , and A_{ij} is the line integral of the vector potential along the bond (ij) ; the sum of the A_{ij} taken in a clockwise direction over the bonds forming an elementary plaquette of the lattice is fixed to be $\sum_{\square} A_{ij} = 2\pi f$ for each plaquette ($f \in [0, 1/2]$). The frustration parameter f is simply related to the square of the amplitude of the uniform applied field (see above). By duality transformation [72], one may alternatively focus on the associated defect (vortex) description: this corresponds to a 2D Coulomb lattice gas in a uniform background charge $-f$, whose Hamiltonian is just the lattice version of equation (11).

Simulations of the 2D uniformly frustrated XY model and of the associated Coulomb lattice gas model have been performed for a large value of frustration, $f_* = (3 - \sqrt{5})/2$, corresponding to the so-called ‘full frustration’, and glassy behaviour reminiscent of supercooled liquids has indeed been observed [73, 74].

In three dimensions, one can generalize the Coulomb lattice gas to a lattice model of interacting vortex loops, in which vortex lines are forced by frustration in all directions of space (as is required to model a glass-forming liquid, but no longer corresponds to an extreme type-II superconductor in an applied magnetic field [75]):

$$H = \frac{J}{2} \sum_{i,j,\mu=x,y,z} (s_{i\mu} - f) G(|\mathbf{x}_i - \mathbf{x}_j|) (s_{j\mu} - f) \quad (13)$$

where $s_{i\mu}$ is the integer vorticity on bond μ emanating from site i , which forms continuous lines (loops or infinite lines), and $G(|\mathbf{x}_i - \mathbf{x}_j|)$ is the lattice 3D Coulomb interaction that goes as $1/|\mathbf{x}_i - \mathbf{x}_j|$ at large separations. Charge neutrality imposes that $\sum_{i,\mu} (s_{i\mu} - f) = 0$.

At this point one should stress that whereas structural and thermodynamic properties are simply obtained by studying the partition function computed by integrating over the defect degrees of freedom, the dynamics is trickier: the mapping from the local order parameter, which evolves with simple local dynamics, to the associated defects may imply quite complex kinetic rules for the defects (see section 8.2).

4.3. Competition between effective interactions: (screened) Coulomb frustrated models

Frustration describes a competition between a local tendency to order and opposing constraints. It is then tempting to describe this situation at a coarse-grained level by means of competing effective interactions acting on different length scales. The situation seems quite clear for the ordering tendency: the corresponding interaction is short-ranged and the associated local order parameter characterizes the liquid LPS. Although things are not as clear as far as the frustrating effective interaction is concerned, there is a good rationale for taking this interaction as long ranged. This is what we argue now.

⁷ We focus here on models in which frustration can be continuously tuned. We do not consider uniformly frustrated spin models where frustration results from the geometry of the lattice, such the already mentioned antiferromagnetic Ising model on a triangular lattice. Such systems usually display a large degeneracy of the ground state, a complex phase diagram, and other interesting phenomena [112], but we do not think they are directly relevant to the glass transition problem.

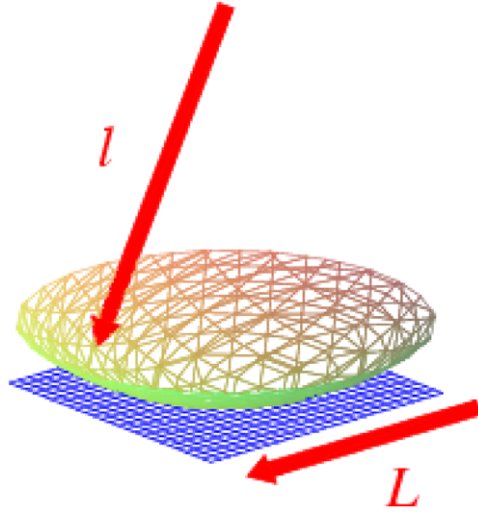


Figure 6. ‘Squashing’ of an ideally ordered region of size L from curved space to flat space; l denotes the intrinsic curvature (i.e., frustration) scale.

A robust feature of the effect of frustration is the fact that, at low temperature, forcing the extension of the LPS (i.e., the ideal order) over a region of size L induces a super-extensive free-energy cost, a strain energy in a continuum elastic picture, that grows as L^{d+2} in dimension d . A heuristic and somewhat simple-minded argument can be put forward as follows. Imagine a reference curved space with intrinsic curvature scale ℓ which is (ideally) ordered at low temperature (see figure 6). What is the effect of ‘squashing’ an ordered region of size L , with L much larger than the typical molecular size but smaller than ℓ (this implies that frustration is small), onto flat, Euclidean space? The free-energy density of this region in flat space can be expanded as

$$\Phi(L, l) = \Phi_0(l) + \Phi_1(l) \left(\frac{L}{l} \right) + \Phi_2(l) \left(\frac{L}{l} \right)^2 + O \left(\left(\frac{L}{l} \right)^3 \right). \quad (14)$$

The first term of the above expression corresponds to the free-energy gain associated with ideal ordering in the absence of frustration ($\Phi_0(\ell) < 0$); the second term is zero, $\Phi_1(\ell) = 0$, because one can choose the flat region locally tangent to the curved space. The last term describes the dominant contribution to the cost generated by frustration. As a result, the corresponding contribution to the free energy of the region of volume L^d in flat space goes as $(\Phi_2(\ell)/\ell^2)L^{2+d}$ for a space of dimension d . This ‘super-extensive’ cost prevents the extension of the LPS in Euclidean space.

The argument can be checked on the models described in the two above subsections. The two-dimensional case is straightforward. Consider the free-energy functional described in equations (6), (7). In this case, ideal order consists in a hexatic phase which is present in the unfrustrated Euclidean space and corresponds to a uniform order parameter $\mathbf{n}(\mathbf{x}) = \mathbf{n}_0$. The free energy of a region of size $L \ll \ell = \kappa^{-1}$ with $\mathbf{n}(\mathbf{x}) = \mathbf{n}_0$ on the hyperbolic plane is then given at leading order in $\kappa \ell$ by

$$F = \frac{1}{2} \kappa^4 Z_H |\mathbf{n}_0|^2 \pi \int_0^L r \, dr \, r^2 \sim \kappa^4 L^4, \quad (15)$$

where we have used the fact that at leading order $g_{\mu\nu} \approx \delta_{\mu\nu}$ and $\Gamma_{\lambda\mu}^\nu(\mathbf{x}) = -\kappa^2 \delta_{\lambda\mu} x^\nu$. Here too, and up to possible logarithmic corrections, there is a free-energy cost that grows as L^{d+2}

with $d = 2$. The same reasoning applies to the extreme type-II superconducting film in a perpendicular magnetic field.

In terms of the associated defect picture, with defects being either point disclinations or point vortices, the above result can be simply interpreted: forcing the ideal (hexatic or superconducting) order in a region of size L when frustration is present amounts to forcing the defect density to be zero in that region; due to the Coulombic nature of the interactions in equations (10) and (11), this then leads to a super-extensive cost that goes as $\kappa^4 L^4$ or $f^2 L^4$ (plus logarithmic corrections). A main difference between hexatic order on the hyperbolic plane and superconducting order in a uniform magnetic field is the presence of a screening effect in the former case at distances larger than the intrinsic frustration (curvature) scale.

The three-dimensional case of models with a coupling to a non-Abelian gauge background is slightly more involved. Consider for illustrative purpose the $SO(4)$ theory of frustrated icosahedral order with the local order parameter $\mathbf{Q}_\ell(\mathbf{x})$ with $\ell = 12$ (in the following we drop the index ℓ). Ideal order now exists in curved space. Following the interpretation of Sethna [40] and Nelson–Widom [36], particle configurations in Euclidean space that most closely mimic the ideal order are constructed by ‘rolling’ a reference polytope $\{3, 3, 5\}$ between adjacent points. It is then convenient to introduce a change of variable

$$\mathbf{Q}(\mathbf{x}) = e^{i\kappa \hat{\mathbf{L}}_{0\mu} x^\mu} \tilde{\mathbf{Q}}(\mathbf{x}) \tag{16}$$

so that the order is now measured relative to a reference polytope that has been rolled in straight lines emanating from the origin in all directions. One can then try to force the relation $\tilde{\mathbf{Q}}(\mathbf{x}) = \mathbf{Q}_0$ in a region of linear size L around the origin, with \mathbf{Q}_0 minimizing the potential part of the free-energy functional (i.e., $\frac{1}{2} \tau |\mathbf{Q}(\mathbf{x})|^2 + O(\mathbf{Q}^3)$). The free-energy cost is associated with the gradient term $\frac{1}{2} Z \int d^3x |D_\mu \mathbf{Q}(\mathbf{x})|^2$.

By applying the Baker–Campbell–Hausdorff formula

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]+\frac{1}{12}([A,[A,B]]+[B,[B,A]])+\dots} \tag{17}$$

to

$$e^{i\kappa \mathbf{C}_\mu(\mathbf{x})} = e^{-i\kappa \hat{\mathbf{L}}_{0\mu} x^\mu} e^{i\kappa \sum_\nu \hat{\mathbf{L}}_{0\nu} x^\nu}, \tag{18}$$

where we have made explicit the sums over repeated indices to avoid ambiguity, one obtains that

$$i\kappa \mathbf{C}_\mu(\mathbf{x}) = i\kappa \sum_{\nu \neq \mu} \hat{\mathbf{L}}_{0\nu} x^\nu - \frac{1}{2} (i\kappa)^2 \sum_\nu [\hat{\mathbf{L}}_{0\mu}, \hat{\mathbf{L}}_{0\nu}] x^\nu x^\mu + O(\kappa^3 x^3). \tag{19}$$

The covariant derivative can then be rewritten

$$D_\mu \mathbf{Q}(\mathbf{x}) = e^{i\kappa \sum_\nu \hat{\mathbf{L}}_{0\nu} x^\nu} (\partial_\mu + \Gamma_\mu(\mathbf{x})) \tilde{\mathbf{Q}}(\mathbf{x}), \tag{20}$$

with the ‘connection’ $\Gamma_\mu(\mathbf{x})$ now defined as

$$\Gamma_\mu(\mathbf{x}) = i\kappa \partial_\mu \mathbf{C}_\mu(\mathbf{x}) = -\frac{1}{2} (i\kappa)^2 \sum_\nu [\hat{\mathbf{L}}_{0\mu}, \hat{\mathbf{L}}_{0\nu}] x^\nu + O(\kappa^3 x^2). \tag{21}$$

It is easy to check that the first term of the expression is equal to the covariant curl, $-(i/2) \mathbf{F}_{\mu\nu} x^\nu$, which is non-zero due to the non-Abelian property of the gauge group $SO(4)$; it is also equal to the curvature tensor and in the present case is proportional to the Gaussian curvature κ^2 .

When $\tilde{\mathbf{Q}}(\mathbf{x}) = \mathbf{Q}_0$, the gradient term can be expressed at leading order in $\kappa \ell$ (with the Einstein summation convention again) as

$$\begin{aligned} F_{\text{cost}}(L) &= \frac{1}{2} Z \int_{(L)} d^3x |\Gamma_\mu(\mathbf{x}) \mathbf{Q}_0|^2 \\ &= \frac{1}{8} Z \kappa^4 (\hat{\mathbf{L}}_{\mu\nu} \mathbf{Q}_0)^* (\hat{\mathbf{L}}_{\mu\nu'} \mathbf{Q}_0) \int_{(L)} d^3x x^\nu x^{\nu'}, \end{aligned} \tag{22}$$

where a star denotes complex conjugation and where we have used the commutation relations of the $SO(4)$ generators, $[\hat{\mathbf{L}}_{0\mu}, \hat{\mathbf{L}}_{0\nu}] = i\hat{\mathbf{L}}_{\mu\nu}$. It is trivial to derive from the above equation that the free-energy cost grows as $\kappa^4 L^5$ with some irrelevant prefactor⁸.

If, as argued above, frustration indeed generates a super-extensive free-energy cost opposing the extension of the ideal order, the associated effective interaction should be long ranged: the integral of a Coulombic interaction $\propto 1/r^{D-2}$ over a region of size L in dimension d precisely leads to an energy going as L^{d+2} . Such a Coulomb-like dependence is a very general feature of interactions between defects, be they vertices in superconductors, dislocations in crystals, or disclinations in bond-orientationally ordered phases [43]. Therefore, whereas the extension of the liquid LPS is more conveniently formulated in terms of a local order parameter, frustration is more conveniently formulated in terms of defect densities, akin to local ‘disorder’ parameters. A full-fledged gauge field theory could possibly handle this duality (see above and [43]). However, a much simpler picture is provided by working with a single variable $\mathbf{S}(\mathbf{x})$ for all effective interactions. This leads to (possibly screened) Coulomb-frustrated models. In a continuum description, the associated free-energy functional is given by

$$F[\mathbf{S}] = \int d^3x \left\{ \frac{1}{2} Z |\partial_\mu \mathbf{S}(\mathbf{x})|^2 + \frac{1}{2} \tau |\mathbf{S}(\mathbf{x})|^2 + O(\mathbf{S}^3) \right\} + \frac{1}{2} K \int d^3x \int d^3y \mathbf{S}(\mathbf{x}) G(|\mathbf{x} - \mathbf{y}|) \mathbf{S}(\mathbf{y}), \quad (23)$$

where $K > 0$ is a measure of the frustration strength. $G(|\mathbf{x}|)$ is the Coulomb interaction that behaves as $1/|\mathbf{x}|$ in 3D, possibly screened at distances much larger than an intrinsic frustration length ℓ . (Typically, such a screening leads to a Yukawa pair potential, $\exp(-(|\mathbf{x}|/\ell))/|\mathbf{x}|$.) In the above equation, we have been cavalier with the tensorial character of the variables and the interactions.

One may as well consider a lattice version

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \frac{K}{2} \sum_{i,j} \mathbf{S}_i G(\mathbf{x}_i - \mathbf{x}_j) \mathbf{S}_j \quad (24)$$

which is more convenient for computer simulations. The models are chosen such that in the absence of frustration ($K = 0$) there is a continuous or weakly first-order transition to an ideally ordered phase at a temperature of order J .

In the corrugated-space picture [35, 27, 76], one can interpret the above Coulomb-frustrated models as describing the competition between the extension of the ideal order in regions which look like the reference space, i.e., regions with an effective curvature that allows tiling by the LPS, and the repulsion between regions of alike curvature, which enforces the constraint that the average curvature must be zero (see also [77]).

Models similar to those described here have been used in quite different contexts. In diblock copolymers formed by two mutually incompatible polymer chains attached to each other, the repulsive short-range forces between the two types of components tends to induce phase separation of the melt, but total segregation is forbidden by the covalent bonds that link the subchains together [78–80]. A microphase separation transition occurs instead at low enough temperature and the system then forms periodically modulated phases, such as lamellar, hexagonal, and cubic phases. Similarly, self-assembly in water–oil–surfactant mixtures results from the competition between the tendency of oil and water to phase separate and the

⁸ Notice that the gradient term expressed with the new variable $\tilde{\mathbf{Q}}(\mathbf{x})$ (see equation (21)) is quite similar to that derived for the two-dimensional uniformly frustrated systems, equations (7) and (9). In all cases there is a connection that is akin to a fixed, but now non-uniform, gauge field. The gauge group however is Abelian for superconducting films ($U(1)$), whereas it is non-Abelian in theory of geometric frustration (e.g., $SO(4)$). Topological defects are induced by frustration in all cases, but the consequences of the Abelian versus non-Abelian property must still be investigated.

stoichiometric constraints generated by the presence of surfactant molecules, constraints that act as the electroneutrality condition in a system of charged particles [81–84]. The same kind of physics also arises in a very different situation: stripe formation in doped antiferromagnets like cuprates has been ascribed to a frustrated electronic phase separation, by which a strong local tendency of the holes to phase separate into a hole-rich ‘metallic’ phase and a hole-poor antiferromagnetic phase is prohibited by the long-range Coulombic repulsion between the holes [85].

The behaviour of Coulomb-frustrated models has been studied both through scaling arguments and by computer simulations. The results will be described in sections 6 and 7.

5. Avoided criticality

It seems a little distressing that no unique, unchallenged minimal theoretical model for frustration in liquids has been derived so far. However, the situation is not as bad as it looks, since there appear to be universal or to the least robust properties shared by the models described in the above section. The most important such property is that of ‘*avoided criticality*’ [20, 86, 87]. This notion expresses the fact that the critical point which exists in the absence of frustration and separates a disordered (liquid) from an ideally ordered phase disappears as soon as an infinitesimal amount of frustration is introduced.

Let us try to make this more explicit. Long-range ideal order is forbidden in the presence of frustration, but other types of order, which we generically describe as ‘defect-ordered phases’, are still possible. By defect-ordered phases, we mean phases in which the defects that break the ideal order themselves arrange in a periodic array. This includes Frank–Kasper-like phases in materials with local icosahedral order, in which the disclination lines form a regular network; the Abrikosov flux lattice in type-II superconductors, in which the vortices form a lattice; and in Coulomb-frustrated systems phases with modulated order, in which domain walls arrange in regular patterns leading for instance to lamellar or stripe phases. The phenomenon of avoided phase transition then means that the limit to zero frustration of the possible transitions to these defect-ordered phases is at a temperature T_{DO} (frustration $\rightarrow 0^+$) significantly lower than $T_c^{(0)}$, that of the critical point in zero frustration. This discontinuity, which is illustrated in figure 7, is a genuine non-perturbative effect due to the strong fluctuations generated by frustration. A similar phenomenon occurs if the transition at $T_c^{(0)}$ is weakly first order [57]. (For a strong first-order transition, the transition may also be avoided, but the associated phenomenology is different [88].) It is worth stressing that this property of avoided criticality has been overlooked in earlier studies of geometric frustration [26, 38].

5.1. Evidence for avoided criticality in the frustrated models

We first discuss the cases where frustration is described either through a coupling to a non-Abelian gauge background or by an effective Coulomb interaction. Proving the existence of an avoided critical point then implies several steps.

The first step is to show that the minimum of the interaction kernel $\Delta(|\mathbf{x} - \mathbf{y}|)$, or in Fourier space $\Delta(q)$, which appears in the quadratic part of the free energy functional, i.e., in

$$F[\mathbf{S}] = \frac{1}{2} \int \frac{d^d q}{(2\pi)^d} \mathbf{S}(-\mathbf{q}) \Delta(q) \mathbf{S}(\mathbf{q}), \quad (25)$$

or a similar expression for the models defined in (equation (3)), occurs at a non-zero wavevector with modulus q_0 . In the Coulomb frustrated models (equation (23)), the interaction kernel can be expressed as

$$\Delta(q) = q^2 + (4\pi K)/q^2 + \text{constant}, \quad (26)$$

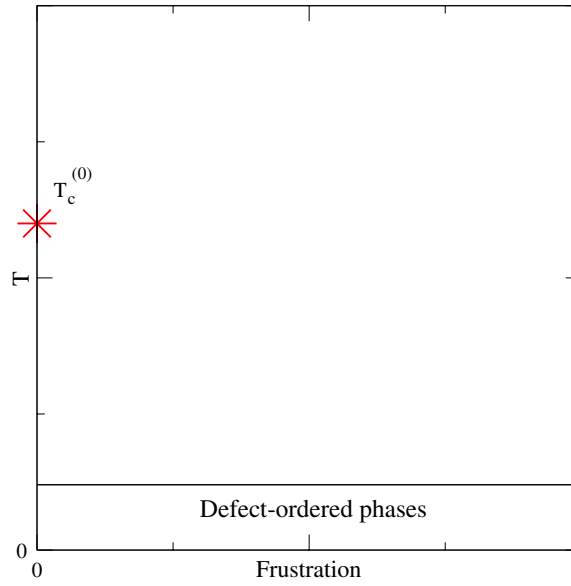


Figure 7. Schematic temperature–frustration diagram illustrating the property of avoided criticality (a genuine discontinuity when frustration goes to zero) between the transition in zero frustration at $T_c^{(0)}$ and the possible transition to defect-ordered phases indicated by the full line.

where we have used that the Fourier transform of the Coulomb interaction is equal to $4\pi/q^2$; the minimum then occurs for $q_0 = (4\pi K)^{1/4}$ (here and in the following we have set for convenience $Z \equiv 1$). In the screened Coulomb case, the above result is modified to

$$\Delta(q) = q^2 + \ell^{-2} + (4\pi K)/(q^2 + \ell^{-2}) + \text{constant}, \quad (27)$$

with the minimum now at $q_0 = (4\pi K - \ell^{-2})^{1/2}$. For physical reasons (see section 4.3), one expects the coupling parameter K to be related to the inverse of the frustration length, $K \sim \ell^{-\varpi}$, so that the minimum is again at a nonzero wavevector whenever $0 < \varpi \leq 4$.

For the models with a coupling to a gauge background, the demonstration is more involved. The interaction kernel in Fourier space is not only a function of q but also an operator or a matrix that should be diagonalized. It can be checked in the $SO(4)$ theory of Nelson and co-workers (see equations (1) and (2)) that all the eigenvalues $\lambda_{mm'}^\ell(q)$ of the kernel, associated with a given representation of dimension $(\ell + 1)^2$ of $SO(4)$, have a single minimum at a non-zero value $q_{0,mm'}^\ell$ that goes as κ for small κ (where κ is the coupling strength associated with geometric frustration): see for instance figure 6 of [38]. In figure 8 we also plot as another example the eigenvalues for the simpler case of $O(4)$ spins with $SO(4)$ couplings in three dimensions [57].

The second step consists in studying the models in the limit where the number of components N of the local order parameter is large. Exact analytic results can be obtained when $N \rightarrow \infty$ [86] (this corresponds to the spherical limit for hard spins and to the Gaussian variational or Hartree approximation for soft spins). A phase transition (of second order in this case) occurs whenever

$$-\tau = \int \frac{d^d q}{(2\pi)^d} \frac{1}{\lambda(q) - \lambda(q_0)}, \quad (28)$$

where τ is defined in equations (3) and (23) and $\lambda(q)$ is the smallest of the eigenvalues of the interaction kernel. A similar expression can be derived for a lattice, hard-spin version [86]. It

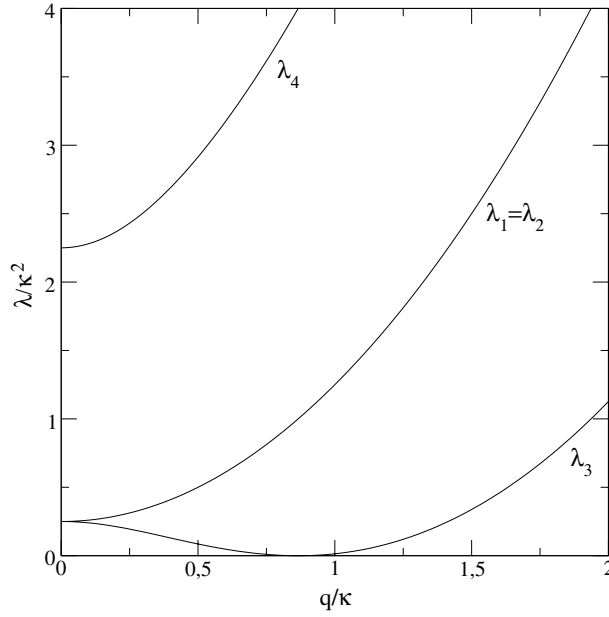


Figure 8. Eigenvalues of the quadratic part of the Hamiltonian describing $O(4)$ spins with non-Abelian $SO(4)$ couplings in three dimensions in the continuum limit (see text). There are four eigenvalues, $\lambda_1 = \lambda_2 = \mu - 6 + \kappa^2 + q^2$, $\lambda_{3,4} = \mu - 6 + 2\kappa^2 + q^2 \mp \kappa\sqrt{\kappa^2 + 4q^2}$, where κ is the frustration strength and μ is chosen so that the minimum value of the lowest eigenvalue is equal to zero. From top to bottom, λ_4 , $\lambda_1 = \lambda_2$ and λ_3 divided by κ^2 , plotted as a function of the dimensionless wavevector (q/κ). The minimum in λ_3 occurs on a shell $q_0/\kappa = \sqrt{3}/2$.

is easy to check that the integral on the right-hand side is dominated by wavevectors whose modulus q is near q_0 ; in this domain, the denominator can be approximated by a quadratic term proportional to $(q - q_0)^2$ whereas the integration measure is proportional to $dq q_0^{(d-1)}$, so that when $q_0 \neq 0$ the integral strongly diverges in all dimensions d . Therefore, no ordering transition is possible at finite τ , i.e., at non-zero temperature.

When the model is considered on a lattice and not in continuum space, symmetry-breaking effects are generated that may induce a transition at a non-zero temperature. However, in dimension $d < 4$ this temperature is of the order of the magnitude of the symmetry-breaking terms, quite different from and lower than the critical temperature $T_c^{(0)}$ in the unfrustrated system [86]. This leads to the phase diagram illustrated in figure 7. $1/N$ corrections have also been computed and shown to leave unchanged the avoidance of the critical point [87].

As a third step, one can go beyond the large- N limit (note however that the dimension of the main component of the order parameter for local icosahedral order in Nelson’s $SO(4)$ theory is equal to 169, quite a large value) and evaluate the magnitude of the fluctuations about the putative ordered ground state. This can be done in the usual and somewhat heuristic way by studying the quadratic fluctuations only. If the number of components N of the local order parameter is large enough, one always finds ‘transverse’ fluctuations whose size is given by the same integral as that on the right-hand side of equation (28). Because of the strong divergence of the integral, the ground state is always unstable with respect to such transverse fluctuations: as a result, no ordering takes place at finite temperature as soon as frustration is present [57, 87]. In the Coulomb frustrated models, this is what occurs for $N > 2$. For $N = 2$, the divergence of the integral is only finite-temperature logarithmic, which suggests that a phase with quasi-long-range order is possible [87].

The case $N = 1$ (Ising), as more generally the case of all models with a discrete instead of a continuous symmetry, is also special. As first shown by Brazovskii [89] and further supported by computer simulations [90, 91], there is a first-order transition to modulated phases; this first-order transition is induced by the strong fluctuations associated with frustration (indeed the mean-field approximation predicts a second-order phase transition) and its temperature T_{DO} goes continuously to $T_c^{(0)}$ as frustration goes to zero. However, the limit of stability (spinodal) of the disordered phase is depressed to zero temperature and the critical point at $T_c^{(0)}$ remains the only finite-temperature critical point in the temperature–frustration diagram. The transition at T_{DO} being first order, it should be possible in principle to supercool the disordered (liquid) phase to lower temperature. This will be discussed in more detail in section 7.

The above reasoning can be made more rigorous with the help of a generalized Mermin–Wagner inequality [57, 92]; it shows that whenever the integral

$$\int \frac{d^d q}{(2\pi)^d} \frac{1}{\lambda(|\mathbf{q} + \mathbf{q}_0|) - \lambda(|\mathbf{q} - \mathbf{q}_0|) - 2\lambda(q)} \quad (29)$$

diverges, ordering at wavevector \mathbf{q}_0 is inhibited at finite temperature.

Finally, some results are also available concerning the uniformly frustrated spin models. In the two-dimensional version (equations (8) and (9)), there appears to be an avoided critical point, just like in the models described above. In this case, the defect-ordered phases are the Abrikosov vortex lattice and the associated hexatic vortex phase, and vanishing frustration means vanishing applied magnetic field. As shown by Fisher [71] on the basis of the continuum Coulomb gas description (equation (11)) within the KTNHY theory of two-dimensional melting (for a review, see [93]), the transitions to the defect-ordered phases occur, in the limit of vanishing frustration, at temperatures more than an order of magnitude lower than the Kosterlitz–Thouless transition [94, 95] that takes place at zero frustration/zero magnetic field; this has also been confirmed by computer simulations [69, 70, 96]. The resulting phase diagram, as illustrated by figure 1 in [71], is then similar to that shown here in figure 7.

Again, the physics of the transitions in the presence and in the absence of frustration is very different. The melting transitions describe the unbinding of the dislocations and disclinations that are present in the low temperature lattice or hexatic phases formed by the vortices induced by the applied magnetic field. On the other hand, the Kosterlitz–Thouless transition at $T_c^{(0)}$ describes the unbinding of a neutral assembly of vortices of both positive and negative signs. The three-dimensional version describing an extreme type-II superconductor in an applied field does not seem to have an avoided critical point [97, 98], but the case of an isotropic frustration discussed above in section 4.3 has not been studied.

5.2. Consequences of an avoided critical point

In dimension $d > 1$ an Ising ferromagnet, when placed in a uniform external field, has of course some sort of avoided criticality: an infinitesimal field destroys the critical fluctuations beyond a given length scale. However, the phenomenon is trivial. The external magnetic field induces a non-zero magnetization at all temperatures, so that the system is always ferromagnetic and does not undergo any phase transition.

Quite different is the situation in a ferromagnet with N -component vector spins (and $O(N)$ symmetry) in the presence of a quenched random field (with zero mean). For dimensions between 2 and 4, the pure system (no random field) possesses a critical point associated with the usual transition from paramagnetism to ferromagnetism, whereas the random-field model, provided $N \geq 3$, has no phase transition at all and stays paramagnetic at all temperatures [99]; indeed, the lower critical dimension is $d = 2$ in the former case and $d = 4$ in the latter.

Interesting, non-trivial scaling properties emerge in such a case for temperatures equal to and less than $T_c^{(0)}$, the critical point of the pure system [99]. It is to such a phenomenon that we refer when exploiting the property of avoided criticality shown by frustration-based models of glass-forming liquids.

On general grounds, one expects that the presence of an ‘avoided critical point’ leads to several diverging length scales, according to whether one approaches the critical point at zero frustration by varying the temperature, or approaches the critical point or the ideally ordered phase by decreasing the frustration to zero. A phenomenological scaling approach will be developed and discussed in the next section.

6. Phenomenological scaling approach of glass-forming liquids: frustration-limited domain theory

The above developments suggest two main conclusions concerning the description of glass-forming liquids [20].

- (1) Frustration naturally leads to collective (or cooperative) behaviour on a mesoscopic scale, a feature that we have stressed as being characteristic of the phenomenology (see section 2). The collective property comes from the phase growth (in which the liquid LPS spreads in space) induced by the proximity of an avoided critical point, whereas the limitation on the scale over which such a growth can take place results from frustration that aborts the phase transition and leads to ‘avoided criticality’.
- (2) The relevant temperature about which one can organize a scaling description of the viscous slowing down and other collective properties of supercooled liquids is that of the avoided critical point in the associated unfrustrated system. This, of course, is only meaningful if the critical point is narrowly avoided, which implies that the frustration characterizing the liquid under consideration is small enough. Note also that in a liquid the temperature $T_c^{(0)}$ marks a crossover, not a true transition, so that it is not expected to be sharply defined.

6.1. Heuristic scaling arguments

As a first step towards a scaling analysis, one can simply incorporate the physics of frustration-induced avoided criticality in the consideration of aborted nucleation of the ideal ordered phase in the liquid phase. At temperatures sufficiently below $T_c^{(0)}$, the free energy of a single domain of the ideal phase in a disordered liquid environment, when its characteristic linear size is L , can be written as [20, 100]

$$F(L, T) = \sigma(T)L^\theta - \phi(T)L^3 + s(T)L^5. \quad (30)$$

The first two terms are those commonly encountered in classical nucleation theory: the first one represents the free-energy cost associated with building a domain of one phase in another; for simplicity, and in the absence of more specific information, we set $\theta = 2$, which corresponds to a surface tension term associated with the interface between the two phases⁹. The second term is the bulk free-energy difference between the two phases and corresponds to a gain in free energy. If ξ_0 is the correlation length of the unfrustrated system, the surface tension σ scales as ξ_0^{-2} and the ordering bulk free-energy density ϕ as ξ_0^{-3} . The last term represents the strain free energy resulting from the effect of frustration; as discussed in section 4.3, it is

⁹ One of the weaknesses of the scaling approach so far developed for frustration-induced avoided criticality is the elusiveness concerning the nature of the order variable and its coupling to the fluctuations of the main observables such as the one-body density or the dipole density. Some of the assumptions, e.g., $\theta = 2$, are easily justified if the relevant variable has a discrete symmetry, but as discussed in section 4 this discreteness is by no means obvious.

generically expected to grow super-extensively with system size, as L^5 in $d = 3$. The above equation assumes that the size L is large compared to the typical molecular length, so that a continuum, thermodynamic-like description can be used, but is small compared to the intrinsic characteristic scale of frustration, so that one does not have to account for the screening effect that modifies the super-extensive growth of the strain free energy at long distances.

Because frustration in a liquid should be the same at any point of space, one actually expects, instead of the formation of a single domain, the breaking up of the liquid into a collection of domains, or, to use more pictorial terms, a ‘mosaic’ [17] or a ‘patchwork’ [101] of domains. These domains are separated from each other by ‘interfaces’, i.e., regions in which the ideal order is broken and a higher concentration of defects, such as disclination lines, is present. The size of the domains and their further growth when lowering the temperature is limited by frustration. Assuming that the inter-domain interactions are sufficiently weak to be treated by a mean-field approach, the free-energy density, $\Phi(L, T)$, for a domain of linear size L in a mosaic of frustration-limited domains (with randomly oriented local order parameters) can be directly derived from the free energy of a single domain given above, namely [47]

$$\Phi(L, T) = \frac{\sigma(T)}{L} - \phi(T) + s(T)L^2, \quad (31)$$

where σ , ϕ , and s are only trivially renormalized with respect to their values for an isolated domain.

The typical domain size L^* is obtained by minimizing the free-energy density given above, and this leads to $L^*(T) \sim (\sigma/s)^{1/3}$; the strain coefficient s is, however, *a priori* unknown. The scaling analysis thus relies on (at least) two supermolecular structural lengths, the correlation length of the unfrustrated system, $\xi_0(T)$, and the typical domain size, $L^*(T)$. As one decreases the temperature below $T_c^{(0)}$, $\xi_0(T)$ *decreases* whereas $L^*(T)$ is expected to *increase*. Scaling only makes sense below a temperature $T_1 \lesssim T_c^{(0)}$ at which $\xi_0(T)$ and $L^*(T)$ are comparable to each other and both larger than the typical molecular length. Such conditions may be only marginally satisfied in real liquids.

It is important to stress that the mosaic of frustration-limited domains is an equilibrium feature (in the supercooled liquid phase it is of course metastable with respect to the actual crystal): the domains, as well as the overall pattern they form, are not frozen but continuously changing due to molecular motion; their statistical properties, however, depend only on the thermodynamic state of the liquid.

In such a mosaic of domains, α relaxation and flow must involve restructuring of domains. In the simplest scaling picture, the typical free-energy barrier to be overcome for such a restructuring, $\Delta E^*(T)$, scales as $\sigma(T)L^*(T)^2$, i.e., involves motion, creation, or destruction of a domain wall. A more detailed argument for such a description has been given by Stillinger in terms of a ‘tear and repair’ mechanism [101]. Scaling about a narrowly avoided critical point then implies that both $\sigma(T) \propto \xi_0(T)^{-2}$ and $L^*(T)$ have a power-law behaviour in $(T_c^{(0)} - T)$ for temperatures less than $T_c^{(0)}$. (Recall that at and above $T_c^{(0)}$ there are no frustration-limited domains.) As a result, the typical free-energy barrier for α relaxation scales as

$$\Delta E^*(T) \sim (T_c^{(0)} - T)^\psi. \quad (32)$$

In a naive, mean-field-like picture, $\sigma(T)$ and $L^*(T)$ vanish as one approaches $T_c^{(0)}$ from below in an analytic way, $\sigma(T) \propto (T_c^{(0)} - T)$ and $L^*(T) \propto (T_c^{(0)} - T)$, so that one obtains $\psi = 3$. In a more elaborate, but still heuristic (see footnote 5) description, it has been found that $L^*(T)$ goes as $K^{-1/2}\xi_0(T)^{-1}$, where K is the relative amplitude of the frustrating interaction [20] (see equations (23), (24)): the typical domain size then grows as $(T_c^{(0)} - T)^\nu$, where ν is the correlation length exponent of the unfrustrated system, as temperature decreases; it also increases as frustration decreases and diverges in the limit of zero frustration as expected

in a scenario of avoided criticality. Taking $\nu \approx 2/3$, which is characteristic of ordinary critical phenomena in the absence of quenched disorder in three dimensions, one arrives in this case at $\psi \approx 8/3$.

The above estimates concern the collective contribution to the free-energy barrier for α relaxation, that due to the frustration-limited domains which vanish around and above $T_c^{(0)}$. One must also account for the molecular contribution which characterizes ‘ordinary’ liquid behaviour (typically, above the melting temperature T_m). The simplest description that provides a reasonable fit to the experimental data in the ordinary liquid phase without introducing any spurious singularities is a plain Arrhenius formula,

$$\tau_0(T) = \tau_\infty \exp\left(\frac{E_\infty}{k_B T}\right), \quad (33)$$

where τ_∞ and E_∞ are species-specific molecular constants characteristic of the high-temperature liquid.

The main prediction of this scaling approach is thus that the α -relaxation time and the viscosity have an activated-like dependence on temperature, with a *crossover* from molecular, ordinary liquid behaviour to collective, domain-dominated behaviour around $T^* \approx T_c^{(0)}$, a crossover that leads to a change from Arrhenius-like to super-Arrhenius T -dependence,

$$\tau_\alpha(T) = \tau_\infty \exp\left(\frac{E(T)}{k_B T}\right), \quad (34)$$

with $E(T) = E_\infty + \Delta E^*(T)$. The super-Arrhenius contribution to the activation free energy is described by a universal power law,

$$\Delta E^*(T) = \begin{cases} 0 & \text{for } T > T_c^{(0)}, \\ B k_B T_c^{(0)} \left(1 - \frac{T}{T_c^{(0)}}\right)^\psi & \text{for } T < T_c^{(0)}. \end{cases} \quad (35)$$

This prediction fits well the extant experimental data on glass-forming liquids with ψ in the range from $7/3$ to 3 (the best overall fit being for $\psi = 8/3$) [20, 4], a range compatible with the above estimates. This is shown in figure 9. In the fitting procedure, $T_c^{(0)}$ is an adjustable parameter: for virtually all liquids studied, its value is found to be slightly above the melting point T_m ; this indeed makes sense since one expects the stability of the ideal ordered phase in the unfrustrated system at $T_c^{(0)}$ to be higher than that of the actual crystal in the frustrated liquid [56, 57].

The parameter B in equation (35) is a measure of the departure from Arrhenius behaviour, hence of ‘fragility’. From the scaling analysis, we obtain that B increases as frustration decreases (it goes as K^{-1} for Coulomb frustrated models). One can thus associate a large fragility with a small frustration. This is compatible with the view developed in section 3 that atomic glass-formers made of spherically symmetric particles are not fragile, or in the standard terminology are rather ‘strong’, despite the weakness of the inter-particle interactions: frustration in those systems characterized by local icosahedral order is indeed strong.

6.2. Further dynamic and static scaling analysis

It is tempting to push further the scaling analysis in order to address other aspects of the phenomenology of supercooled liquids.

The equilibrium distribution of domain sizes in the mosaic, $\rho(L, T)$, at temperatures below $T_1 \lesssim T_c^{(0)}$ can be obtained from $\rho(L, T) \propto \exp[-(\Phi(L, T) - \Phi_*(T))L^3/k_B T]$, where

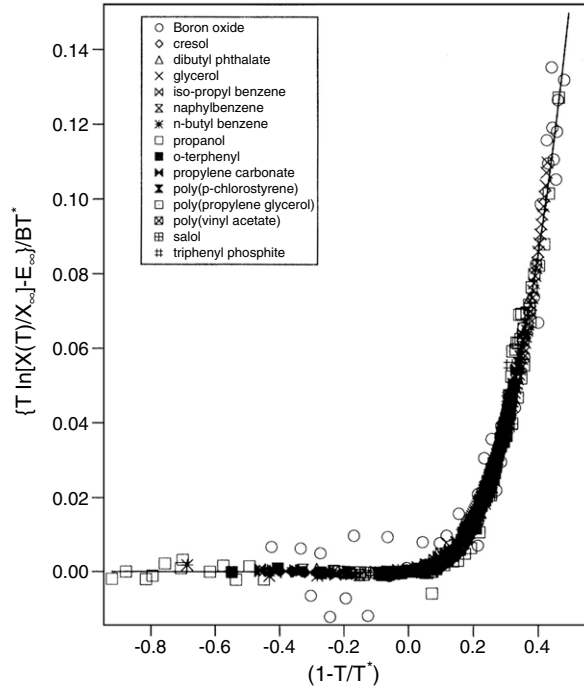


Figure 9. Scaling of the collective component of the effective activation (free) energy, $\Delta E^*(T)$, versus reduced temperature $(T^* - T)/T^*$ measured from the crossover temperature T^* (or equivalently, the avoided critical temperature $T_c^{(0)}$). The solid line is the 8/3 power law discussed in the text. Reprint with permission from [4], copyright by the American Physical Society.

$\Phi(L, T)$ is the free-energy density given in equation (31) and $\Phi_*(T)$ its value at the minimum. It can be cast in a scaled form as [47, 102]

$$\rho(L, T) \propto \exp \left\{ -\gamma(T) \left[\kappa \left(\frac{L}{L^*} \right)^2 - \frac{3}{2} \left(\frac{L}{L^*} \right)^3 + \frac{1}{2} \left(\frac{L}{L^*} \right)^5 \right] \right\}, \quad (36)$$

where the entire temperature dependence is contained in the parameter $\gamma(T) \propto B(T_c^{(0)}/T)(1 - T/T_c^{(0)})^\psi$; κ is a number of order unity introduced to allow for small domain-shape effects at a mean-field level [102] (it should not be confused with the frustration parameter κ used in sections 3 and 4).

By generalizing the simple dynamic scaling arguments presented in the above subsection, one can also evaluate the collective contribution to the activation free energy, $\Delta E(L, T)$, for a domain of size L ; this latter takes the following scaled form [47, 102]:

$$\frac{\Delta E(L, T)}{k_B T} = b\gamma(T) \left[\left(\frac{L}{L^*} \right)^2 - m \left(\frac{L}{L^*} \right)^5 \right], \quad (37)$$

where b and m are numbers of order unity, with $bm < 1/2$. The last term in L^5 has been included to account for the fact that building or moving a domain wall costs a free energy of order σL^2 but leads to a reduction in strain free energy. The full effective activation free energy is then obtained by adding the molecular, Arrhenius-like contribution, $E_\infty/k_B T$, to the above expression.

Below the temperature $T_1 \lesssim T_c^{(0)}$ at which the liquid breaks up into supermolecular domains, the dynamics are naturally described as *heterogeneous*. For instance, the

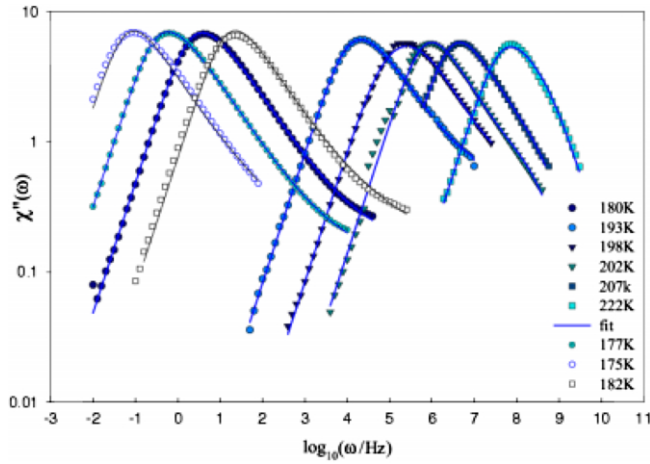


Figure 10. Frequency-dependent dielectric susceptibility of the fragile glass-former m -fluoroanilin for several temperatures on a log–log plot: comparison between experimental data ($T_g = 172$ K) and frustration-limited domain scaling theory (data and fits by Alba-Simionesco, see also [103]). The parameters used for the fit (see the text) are $T^* = T_c^{(0)} = 258$ K, $E_\infty = 1587$ K, $\tau_\infty = 10^{-12}$ s, $\kappa = 0.62$, $m = 0.29$, $b = 1.04$, $B = 364$. The exponent ψ is fixed to $8/3$.

nonexponential character of the dielectric relaxation can be simply modelled by assuming that molecular reorientations are completed within a single domain, in which they are dynamically coupled to the order variable, and by assuming that the relaxation within each domain is exponential in time [9]. (Of course, there may be systems such as polymers for which the bare ‘molecular’ relaxation is already non-exponential; the collective behaviour associated with the mosaic of domains then increases the non-exponential character.) This leads to the following expression for the normalized dielectric relaxation function [47, 102]:

$$f_\alpha(t) = \int_0^\infty dL L^2 \rho(L, T) \exp\left[-\frac{t}{\tau_\infty} \exp\left(-\frac{E_\infty + \Delta E(L, T)}{k_B T}\right)\right], \quad (38)$$

with $\rho(L, T)$ and $\Delta E(L, T)$ given in equations (36) and (37). The above expressions compare well with experimental data on glass-forming liquids [102]. This is illustrated in figure 10, where the imaginary part of the frequency-dependent dielectric susceptibility of the fragile glass-former αm -fluoroanilin is compared to the Fourier transform of $df_\alpha(T)/dt$ obtained from equations (36)–(38): the main features of the α relaxation are well reproduced over a large frequency range (up to 13 decades) and a large temperature domain [103]. (The approximate scaling plot proposed by Nagel and co-workers [104] is also well reproduced [47, 102].) One of course recovers for the temperature dependence of the peak frequency the power-law behaviour described in equation (35). The number of adjustable parameters strongly restricts the predictive power of the scaling approach, but it should be stressed that these parameters are *independent of temperature*. From these parameters one can estimate the typical domain size, which is found to be around 5–10 molecular diameters at T_g , an estimate that is compatible with experimentally determined sizes (see section 3); with additional input [105], one can also describe the decoupling between translational diffusion and reorientational relaxation [102].

A couple of additional points are worth stressing.

- (i) In this approach, the heterogeneous character of the α relaxation in the supercooled liquid regime is a consequence of a *structural* property, namely, the break-up of the liquid into

a mosaic of frustration-limited domains; this is to be contrasted with other descriptions that focus on purely kinetic mechanisms (see the review article [106]).

- (ii) The super-Arrhenius growth of the relaxation time with decreasing temperature is accompanied by only a modest stretching of the relaxation functions (compare for instance with the quite different behaviour of magnetic systems in the presence of a random field [107]); in the present scaling description, this results from the decreasing polydispersity of the domains as temperature decreases.

Finally, scaling about an avoided critical point gives a qualitative account of the rapid decrease of the excess (or ‘configurational’) entropy observed in supercooled liquids as one approaches the glass transition. Within this approach, there are indeed two sources of entropy decrease below $T_c^{(0)}$ as one lowers the temperature: the first one is the increase of ordering that should take place inside all the domains [108]; the second is associated with the growth of the typical domain size and the resulting decreasing weight of the interfaces with high concentration of defects. This latter effect will be further discussed in section 8, in connection with the description of glass-forming liquids in terms of the complexity of their free-energy landscape and the large number of metastable states. Just as the α -relaxation time and the viscosity rapidly increase with decreasing temperature with no need for a low-temperature singularity, the frustration-limited domain approach predicts a rapid decrease of the entropy with no requirement for a low-temperature Kauzmann catastrophe.

The above phenomenological scaling analysis illustrates how the concept of frustration coupled with the property of avoided criticality can provide a framework for describing the phenomenology of glass-forming liquids. However, whether or not the assumptions that underlie the scaling analysis evolve rigorously from the statistical–mechanical models discussed in section 4 remains a fundamental theoretical uncertainty. This point has not yet been resolved, but some progress has been achieved by means of computer-simulation studies of simple frustrated models. This is what we discuss next.

7. Computer simulations of simple systems: Coulomb frustrated lattice models

The Coulomb frustrated spin models described in section 4.3 seem to be the simplest systems compatible with the frustration-based approach of glass formation. Setting aside the issue of their microscopic derivation, it is possible to check the relevance of the scenario presented above by investigating numerically such models. Extensive Monte Carlo simulation studies [91, 109, 110] have been performed for models on a three-dimensional cubic lattice with Hamiltonian (see also equation (24))

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \frac{K}{2} \sum_{i \neq j} \frac{\mathbf{S}_i \cdot \mathbf{S}_j}{|\mathbf{x}_i - \mathbf{x}_j|} \quad (39)$$

for a variety of spin variables, mostly with discrete symmetry: Ising model, $\mathbf{S}_i = 1$, q -state clock model, $\mathbf{S}_i = (\cos(2\pi\theta_i/q), \sin(2\pi\theta_i/q))$, with θ_i the orientation of the planar spin and $q = 5$ and 11 . We also include here new results obtained for the XY model, i.e., for continuous planar spins.

In the absence of frustration ($Q = 0$), the models have a critical point at a temperature $T_c^{(0)}$, below which they are ferromagnetic. The long-range, Coulombic interaction requires that the total magnetization of the system be zero in order to ensure a proper thermodynamic limit. Therefore, long-range ferromagnetic order is prohibited at all T for any nonzero value of the frustration parameter Q/J . (In what follows, we take $J = 1$.) The models studied

(XY and discrete orientations) display only a ‘weak’ form of avoided criticality. They can still form ordered or quasi-ordered phases characterized by modulated patterns (e.g., lamellar phases) below a temperature $T_{\text{DO}}(Q)$ that goes non-analytically but continuously to $T_c^{(0)}$ as Q goes to zero. However, the transition between paramagnetic and modulated phases is first order [90, 91]. Following Brazovskii [89], this result can be interpreted on the basis of the self-consistent Hartree approximation which predicts the occurrence of a fluctuation-induced first-order transition, a transition with no nearby low- T spinodal. As a result, $T_c^{(0)}$ remains the only nearby (and avoided) critical point in the frustration–temperature diagram. All the simulations have been made in the disordered (paramagnetic) phase. Since the transition to the modulated phases at $T_{\text{DO}}(Q)$ is first order, one could in principle supercool the paramagnetic phase to lower temperatures; however, it has been found that the lattice sizes accessible in practice are too small to allow for a proper supercooling below T_{DO} [109, 110]. This, unfortunately, restricts the domain of temperature over which one can study the slowing down of the dynamics. (Out-of-equilibrium dynamics and aging phenomena have not been considered.)

The relaxation to equilibrium of the frustrated systems has been studied via the Monte Carlo algorithm (Metropolis rule), time being the number of sweeps per spin. The dynamical quantity that has been monitored is the equilibrium spin–spin self-correlation function, $C(t) = (1/N) \sum_i \langle \mathbf{S}_i(t') \mathbf{S}_i(t'+t) \rangle$, where the bracket denotes the thermal average and N is the total number of lattice sites; cubic lattices of size 16^3 to 22^3 with periodic boundary conditions have been used and the Coulomb interaction has been handled via Ewald sums [109, 110].

The evolution of $C(t)$ with T is illustrated in figure 11 for the five-state clock ($Q = 0.1$ and $Q = 0.00625$), the Ising ($Q = 0.001$), and the XY ($Q = 0.005$) models. At the highest frustration, illustrated by figure 11(a), the decay of $C(t)$ appears to proceed in a single step at all temperatures. For lower frustrations, a two-step decay develops as T is lowered (see figures 11(b)–(d)). At high temperature, typically above the critical point of the corresponding unfrustrated model ($T_c^{(0)} \simeq 2.1, 4.51, 2.32$ for the five-state clock, the Ising, and the XY models, respectively), and for all frustrations, the whole time dependence of $C(t)$ is well fitted by a simple exponential, $\exp(-t/\tau_0(T))$. At low temperature, below $T_c^{(0)}$, it is impossible to describe the entire decay of $C(t)$ by a single exponential; the emerging second step of the relaxation can be described by a stretched exponential, $\exp(-(t/\tau_{\text{KWW}}(T))^{\beta(T)})$, while the first step can still be fitted by a simple exponential, $\exp(-t/\tau_0(T))$ [109, 110]. This non-exponential behaviour and emergence of a two-step decay, both of which become more pronounced as T is decreased, are typical of fragile supercooled liquids. One may however notice that the timescale separation between the two relaxation steps that can be achieved in the simulations is not sufficient to observe the development of a true plateau at intermediate times.

The slowing down of the relaxation as one lowers the temperature is visible in figure 12. The temperature dependence of the relaxation times characteristic of the short- and long-time behaviours, $\tau_0(T)$ and $\tau_\alpha(T)$ respectively, has been investigated in [109, 110]. Over the range of temperature studied, the dependence of $\tau_0(T)$ is essentially Arrhenius-like, $\tau_0(T) \simeq \tau_{0,\infty} \exp(E_\infty/T)$, whereas the dependence of $\tau_\alpha(T)$ shows a marked deviation from Arrhenius behaviour below some crossover temperature in the vicinity of $T_c^{(0)}$.

The crossover from Arrhenius to super-Arrhenius behaviour of τ_α is shown in figure 12 for the five-state clock model for several different frustrations. A similar trend is observed for the Ising and XY models. Several points are worth noting: (i) such a super-Arrhenius behaviour is typical of the viscous slowing down of fragile glass-forming liquids, the more fragile a liquid the more pronounced the super-Arrhenius character; (ii) the crossover occurs in the vicinity of the critical point of the unfrustrated system; (iii) the departure from Arrhenius behaviour, i.e., the ‘fragility’, becomes more marked as frustration decreases.

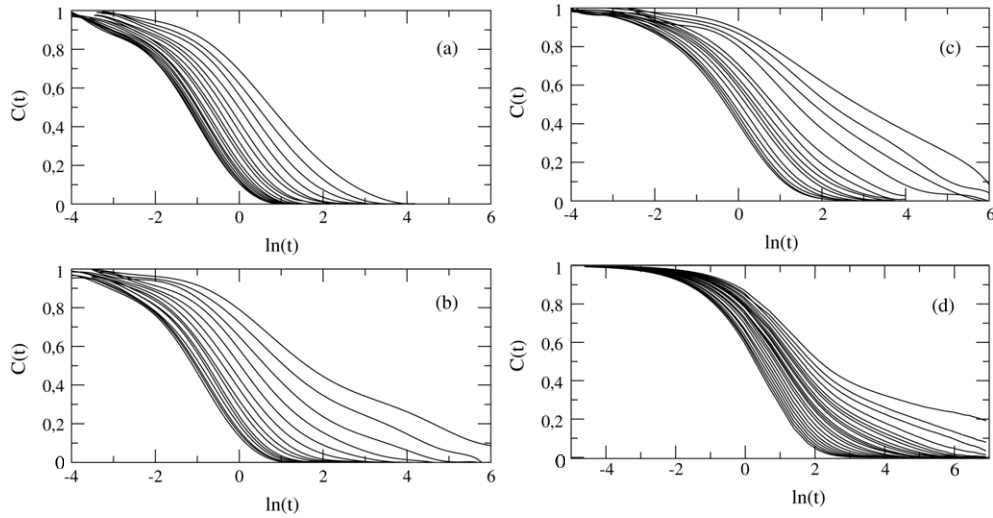


Figure 11. Spin–spin correlation function $C(t)$ versus $\ln(t)$ for several temperatures both above and below $T_c^{(0)}$ (in each panel, curves from left to right are for decreasing temperatures): five-state clock model for $Q = 0.1$ (a) and $Q = 0.00625$ (b); 11-state clock model for $Q = 0.001$ (c); and XY model for $Q = 0.005$ (d).

As shown in [109] and [110], the temperature dependence of the α -relaxation time is compatible with the behaviour predicted by the frustration-limited domain approach (see equation (35)). However, because of the limited domain of temperature, hence the limited range of relaxation times, one should not put too much emphasis on the fit: for instance, the data are also compatible with a Vogel–Fulcher formula, $\tau_\alpha = \tau_0 \exp(DT_0/(T - T_0))$ [111]; on the other hand, they cannot be fitted by a power-law dependence.

Although no direct determination of a domain or heterogeneity length has been attempted in these studies, interesting insight has been provided by investigating the finite-size effect on the relaxation time. As illustrated in figure 13(a), the behaviour is quite different from that of standard critical slowing down (shown here for the unfrustrated system, figure 13(b)): in the presence of frustration, the slowing down of the relaxation does not come with the rapid growth of an associated length, which is compatible with the experimental observations on glass-forming liquids.

The computer simulation studies of Coulomb frustrated spin models thus provide some evidence that such models display many of the main characteristic features of the phenomenology of fragile glass-forming liquids. It is however fair to say (i) that the analogy with supercooled liquids is limited by the range of relaxation times accessible in simulations (due to the presence in those models of a first-order transition to modulated, defect-ordered phases) and (ii) that the mechanisms by which frustration induces a slowing down of the relaxation remain at the level of speculations.

8. Connection to other approaches of the glass transition: complex free-energy landscape and kinetic constraints

So far, we have stressed how frustration provides a physical mechanism for generating cooperative behaviour on a mesoscopic scale, a feature that seems to be at the very root of the phenomenology of fragile glass-forming liquids. We have focused on a generic property

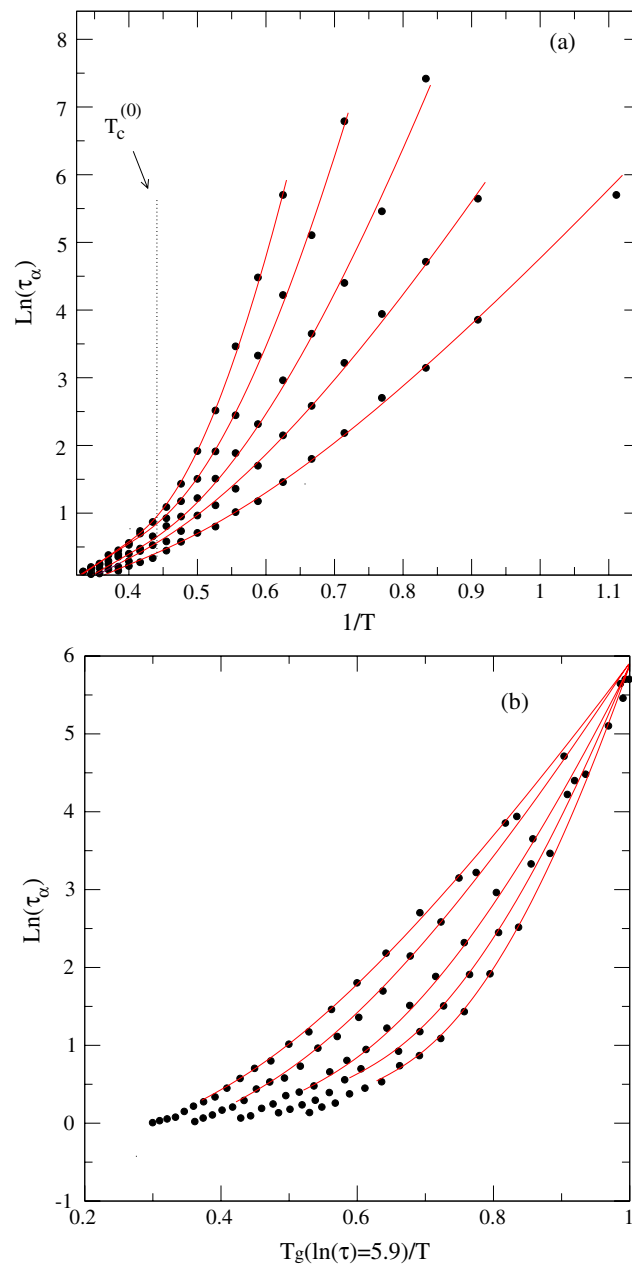


Figure 12. Arrhenius plot of $\tau_\alpha(T)$ for the five-state clock model and various frustrations (from left to right in (a) and from right to left in (b), $Q = 0.00625, 0.00125, 0.025, 0.05, 0.1$). In (b) the curves are plotted versus the reduced inverse temperature $T_g(\ln(\tau) = 5.9)/T$, where $T_g(\ln(\tau) = 5.9)$ is the temperature at which the maximum relaxation time, $\ln(\tau_\alpha) = 5.9$, is attained.

induced by frustration, namely avoided criticality, and on the possibility of developing a scaling approach of supercooled liquids exploiting this property. However, starting from the same statistical mechanical description based on frustration, other routes are possible. It is fruitful

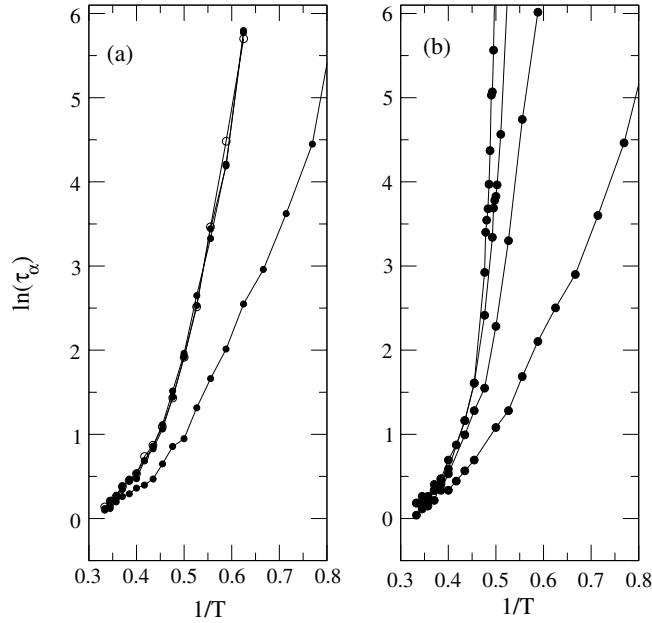


Figure 13. Arrhenius plot of τ_α for the five-state clock model and for lattice sizes $L = 5, 10, 15, 20$ (from right to left): (a) $Q = 0.00625$ (no difference is seen between the three larger sizes) and (b) $Q = 0$ (standard critical slowing down).

to make the connection with other, maybe more common, lines of thought concerning the emergence of glassy dynamics: the ‘landscape paradigm’, which relates the slowing down of the dynamics to the presence of a large number of long-lived metastable states, and the approaches in terms of ‘kinetically constrained models’, in which glassiness results from constraints on the effective kinetics of the system. Whether or not one description is better than the others and to what degree the various approaches are compatible one with another are still, we believe, open questions.

8.1. Long-lived metastable states and complex free-energy landscape

On general grounds, one expects frustration to give rise to a large degeneracy of low-lying energy configurations [23, 112, 27, 26]. A first insight into the presence of long-lived metastable states in supercooled liquids can be gained from a heuristic argument that follows from the phenomenological scaling approach discussed in section 6. If indeed below some temperature $T_c^{(0)}$ a glass-forming liquid splits into a mosaic of frustration-limited domains, if such domains or small groups of domains are characterized by a limited number of long-lived metastable states whose exploration via thermal activation gives rise to the α relaxation, and if these domains are only weakly interacting (see section 6.2), then the system as a whole is characterized by an exponentially large (in system size) number of long-lived metastable states: these states are obtained by combining the metastable states of the roughly independent mesoscopic regions, which does lead to an exponential total number. Since the typical domain size is predicted to increase when either T decreases (at constant frustration) or frustration decreases (at constant T), the number of metastable states is expected to decrease when T or frustration decreases. The logarithm of the number of long-lived metastable states can be used to define a ‘configurational

entropy'. A non-zero 'configurational entropy' thus emerges below the crossover temperature $T_c^{(0)}$ associated with the avoided critical point and decreases as temperature further decreases.

How can one check the above property? The difficulty is twofold. First, a precise definition of a 'long-lived metastable state' must involve a timescale and, as a consequence, cannot *a priori* be treated within a purely static calculation; secondly, one has to find an operational way to compute the number of such metastable states. In the absence of a better solution [113], a way to handle the first aspect is to assume that the long-lived metastable states, if indeed present in the system, have an infinite lifetime: such an approximation, which neglects the thermally activated processes that allow the system to escape from the metastable states and are the source of the α relaxation, has an intrinsic mean-field nature. The other aspect of the problem has found an elegant solution proposed by Monasson [114]: it relies on introducing a weak coupling to a pinning field that prevents the system from sampling all the metastable states (hence breaking ergodicity) and handling the average over the pinning field by means of the replica method, much used in theories of spin glasses and other systems in the presence of quenched disorder [24, 115].

When applied to the models introduced in section 5 to describe frustration in liquids, this 'replica mean-field approach' proceeds as follows [116, 117]. Consider a frustrated model described (in the continuum limit) by the Hamiltonian or free-energy functional $F[\chi]$ ($\chi(\mathbf{x})$ stands for $\mathbf{Q}(\mathbf{x})$ in equation (3), $\mathbf{S}(\mathbf{x})$ in equation (23), etc) and add a weak coupling to a pinning or 'ergodicity-breaking' field $\sigma(\mathbf{x})$. The associated modified partition function is given by

$$\begin{aligned}\tilde{\mathcal{Z}}_\lambda[\sigma] &= \int \mathcal{D}\chi \exp\left[-\beta F[\chi] - \frac{\lambda}{2} \int d^d x (\sigma(\mathbf{x}) - \chi(\mathbf{x}))^2\right] \\ &= \exp(-\beta \tilde{\mathcal{F}}_\lambda[\sigma]),\end{aligned}\quad (40)$$

with $\beta = 1/(k_B T)$ and $\lambda > 0$. If $F[\chi]$ possesses low-lying minima, $\tilde{\mathcal{Z}}_\lambda[\sigma]$ will be large at low temperature when $\sigma(\mathbf{x})$ is close to a configuration of the field $\chi(\mathbf{x})$ corresponding to one of these minima. A weighted average of the free energy in the various metastable configurations is then obtained as

$$\tilde{\mathcal{F}}_\lambda = \int \mathcal{D}\sigma \tilde{\mathcal{F}}_\lambda[\sigma] \frac{e^{-\beta \tilde{\mathcal{F}}_\lambda[\sigma]}}{\int \mathcal{D}\sigma e^{-\beta \tilde{\mathcal{F}}_\lambda[\sigma]}}. \quad (41)$$

When λ is equal to zero, $\tilde{\mathcal{F}}_\lambda[\sigma]$ reduces to the thermodynamic free energy of the system, $\mathcal{F} = -k_B T \ln(\int \mathcal{D}\chi \exp[-\beta F[\chi]])$ and so does $\tilde{\mathcal{F}}_{\lambda=0}$. The behaviour as $\lambda \rightarrow 0^+$ may however be subtle: if the number of metastable states (low-lying minima) is exponentially large in system size, the approach $\lambda \rightarrow 0^+$ is non-perturbative and a discontinuity $\tilde{\mathcal{F}}_{\lambda \rightarrow 0^+} - \tilde{\mathcal{F}}_{\lambda=0}$ is present; the magnitude of the discontinuity is precisely, up to a factor T , the 'configurational entropy', defined as the logarithm of the number of metastable states. Again, this can only happen in a mean-field description, the system in the limit $\lambda \rightarrow 0^+$ being stuck forever in one of the exponentially many metastable states.

The replica trick can now be used to compute the average over the pinning field in equation (41). Defining

$$\beta \mathcal{F}(m) = -\frac{1}{m} \ln \mathcal{Z}(m) = -\frac{1}{m} \lim_{\lambda \rightarrow 0^+} \int \mathcal{D}\sigma \tilde{\mathcal{Z}}_\lambda[\sigma]^m, \quad (42)$$

one obtains after straightforward manipulations that $\tilde{\mathcal{F}}_{\lambda \rightarrow 0^+} = \partial(m\mathcal{F}(m))/\partial m|_{m=1}$ and the configurational entropy, $S_c = \beta(\tilde{\mathcal{F}}_{\lambda \rightarrow 0^+} - \mathcal{F})$ is equal to $\beta \partial \mathcal{F}(m)/\partial m|_{m=1}$, whereas the replicated partition function $\mathcal{Z}(m)$ can be written as

$$\mathcal{Z}(m) = \lim_{\lambda \rightarrow 0^+} \int \prod_{a=1}^m \mathcal{D}\chi_a \exp\left[-\beta \sum_{a=1}^m F[\chi_a] + \frac{\lambda}{2m} \sum_{a,b=1}^m \int d^d x \chi_a(\mathbf{x}) \chi_b(\mathbf{x})\right]. \quad (43)$$

The actual computation of $\mathcal{Z}(m)$ requires of course the introduction of approximations, mean-field-like approximations as stressed above. The first such calculation on a frustrated model has been performed by Schmalian and Wolynes [116] on the Coulomb frustrated model (equation (23)) with an approximation known as the self-consistent screening approximation (SCSA) [118]¹⁰. They find that below a temperature T_A an extensive configurational entropy, i.e., an exponentially large number of metastable states, appears; the entropy decreases as T decreases and becomes negative below a temperature T_K .

These results call for several comments: (1) they confirm the heuristic picture described above and, as expected, T_A is always found below $T_c^{(0)}$, the critical point of the model without frustration; one also obtains that the configurational entropy decreases at constant temperature when frustration decreases. (2) The scenario is similar to that characterizing generalized spin glasses, such as the p -spin of the Potts glass models, in the mean-field limit [115]. In these models, the upper temperature T_A is associated with a dynamic singularity described by the ideal mode-coupling approach whereas the lower temperature T_K corresponds to a *bona fide* thermodynamic transition to a spin-glass phase. It can actually be shown that the temperature T_A in the Coulomb frustrated model is also associated with a dynamic singularity similar to that of the ideal mode-coupling description [119]. One must however recall that this occurs within mean-field approximations and that such a dynamic singularity should vanish in an exact description. The analogy with generalized mean-field spin glasses is the basis of the random first-order transition theory of glass formation developed by Wolynes and his co-workers [17, 18, 120–122]. We shall come back to this theory below.

The same property, namely the appearance of a complex free-energy landscape with an exponentially large number of metastable states¹¹, has been found in other systems related to the frustration-based description of glass-forming liquids, systems in which the minimum of the interaction kernel in Fourier space occurs at a non-zero wavevector q_0 [123, 83, 124, 125]. As discussed in section 5.1, these systems all show the property of avoided criticality. However, most of the studied models are akin to the Ising version (i.e., with a discrete Z_2 symmetry) and display the ‘weak’ form of avoided criticality: a fluctuation-induced first-order transition. We have already mentioned that this transition, whose location is non-universal and model specific, is hard to bypass by supercooling, which limits the accessible domain of temperature in computer simulation studies. As a result, the conclusions concerning the glassy behaviour of the models may not be as clear-cut as one would like and details concerning the parameter range studied may become important: this may explain the apparently conflicting results obtained for the three-dimensional Brazovskii-like model [126, 119, 127, 128]. It seems anyhow that models with a continuous symmetry, like the Coulomb frustrated $O(N)$ model, also follow the same scenario with the emergence of a complex free-energy landscape below the (truly) avoided critical temperature $T_c^{(0)}$ [129].

One may wonder at this point how reliable calculations based on approximations which are to a large extent uncontrolled are. There is of course no definite answer to this question, but one can at least try to check the robustness of the scenario: what happens when improved, or in contrast worse, approximations are used? The approximations being mean field in character,

¹⁰ The SCSA amounts to formally considering an $O(N)$ version of the model under study in the limit of large number of components N , performing a perturbative expansion in $1/N$ and including in a self-consistent manner the leading $1/N$ corrections; one then obtains a coupled set of self-consistent equations for the pair correlation functions of the model. N is then set to the chosen value; in most cases $N = 1$. The same type of approximation can be derived for the dynamics of the system [141, 142].

¹¹ Note that the ground-state entropy in these systems (at least in their large- N behaviour) can be rigorously shown to be proportional to the surface area of the system. The extremely high ground-state degeneracy in these frustrated systems is intimately linked to the existence of a large number of unconventional symmetries [57, 92, 143]. Yet the entropy density goes to zero in the thermodynamic limit.

they may overestimate, as is often the case, the presence of transitions and singularities: are there models for which the approximations do *not* predict the appearance of a complex free-energy landscape? The available answers to these questions tend to support the validity of the scenario. An exponential number of metastable states is also predicted when using an approximation developed for studying strongly interacting systems with predominantly local correlations [130], the ‘dynamic mean-field approximation’ [131]; on the other hand, a number of perturbative treatments cruder than the SCSA mentioned above do not find a complex free-energy landscape [119]. Perhaps more interestingly, when the replica mean-field approach and the SCSA are applied to the three-dimensional model in the absence of frustration, it does *not* find the signature of an exponentially large number of metastable states [114], as indeed expected for a pure ϕ^4 theory.

To conclude this section, it is worth summarizing the main points of the random first-order transition theory of glass-forming liquids [17, 18, 120–122, 19]. In this approach, the mean-field scenario outlined above is modified to include thermally activated escape from metastable states. The dynamic mode-coupling-like singularity is then smeared out to become a crossover to an activation dominated regime associated with the evolution of the system on the complex free-energy landscape. In real space, the liquid is described as a mosaic of cells and activation events as entropic droplets, the driving force for nucleating such droplets being provided by the non-zero configurational entropy. Super-Arrhenius temperature dependence of the α -relaxation time in the form of a Vogel–Fulcher expression is predicted as one approaches the ideal glass transition T_K ; at this point the configurational entropy vanishes and it can therefore be identified with the Kauzmann temperature [11]. This approach successfully describes many aspects of the phenomenology of supercooled liquids.

8.2. Defects and effective kinetic constraints

Topological defects play an important role in frustration-based approaches of glass-forming liquids. In the description of frustrated icosahedral order in three-dimensional space for instance, the most relevant defects are disclinations, i.e., rotational line defects (see section 3). We have also illustrated in section 4 how the statistical mechanical treatment of frustrated systems may become more tractable by going from the original representation in terms of local order parameter to a dual description in terms of topological defects.

It must be emphasized, however, that the simplicity one could gain via such a transformation for studying the structural and thermodynamic properties may have a penalty associated with an increased complexity in the effective equation of motion for the defects. In general, one would have to deal with the kinetics of defect lines in a partially ordered but non-crystalline medium. The slow dynamics of defect lines, such as vortex lines in three-dimensional extreme type-II superconductors, is controlled by crossing, cutting and reconnection, all processes that are thermally activated and may lead to an effective freezing in an entangled ‘glassy’ state on the experimental timescale [132]. Entanglement effects are expected to be especially severe for disclination lines in a frustrated icosahedral medium: in such a case, the underlying theory has a non-Abelian $SO(4)$ symmetry and the resulting combination rules for the defect (disclination) lines have been predicted to lead to non-trivial kinetic constraints [34, 26]. The phenomenological scaling approach reviewed in section 6 side-steps the issue by merely considering quasi-ideally ordered regions (domains) with a low density of defects separated by regions (interfaces) with a high density of defects, without specifying the nature of the defects or their kinetics.

To shed light on the subtle aspects of the duality between the description in terms of local order parameter and that in terms of defects, it is interesting to consider simple models which do not belong to the class of frustrated systems discussed in section 5. They consist

in Ising spin models on two-dimensional lattices, with short-ranged ferromagnetic multi-spin, ‘plaquette’-type, interactions. In the original formulation involving the spin variables, the system is strongly correlated [133, 134] (with trivial pair correlations but non-trivial higher-order ones), and the dynamics is described via local kinetic rules involving one-spin flips. In the dual version in terms of topological defects, the thermodynamics reduces to that of an ideal gas, but the effective dynamics of the defects is now strongly constrained [133–135]).

The presence of kinetic constraints, even in the absence of non-trivial static properties, has been shown to induce a slowing down of the relaxation and, as a result, formation of glassy states on some observation timescale. There is an abundant amount of work on such ‘kinetically constrained models’ (for a review, see [106]), which have been, most notably in recent years [15, 136, 14], advocated as an alternative to thermodynamic approaches for explaining the phenomenology of supercooled liquids. In such descriptions, glassy behaviour is attributed to the emergence of dynamic heterogeneities, with a typical length scale that grows in space–time, but not in space, when temperature is decreased or density increased. The models reproduce many features of glass-forming liquids, with however some shortcomings. In all studies so far carried out, the defects are point-like objects, defects becoming more and more dilute as one approaches the glass transition region; their contribution to the entropy and heat capacity of the liquid (in excess to those of the crystal) is then completely negligible, and the empirical correlation between slowing down of the relaxation and decrease of the ‘configurational’ (excess) entropy observed in liquids approaching their glass transition cannot be described [137, 138]. In addition, the origin of the kinetic constraints is quite elusive.

It is then tempting to speculate, after Palmer *et al* [139], that ‘it is possible to see static frustration over many length scales as the underlying cause of dynamical constraints over many timescales’. Defects could be line-like objects instead of point-like ones, which could help keep the connection between dynamics and thermodynamics. However, no such description has been attempted so far.

9. Conclusion

In this article, we have reviewed the frustration-based approach to supercooled liquids and the glass transition. Frustration in liquids, namely a ubiquitous incompatibility between the spatial extension of the locally preferred liquid structure and the tiling of the whole space, provides a physical mechanism to generate what we have argued to be the distinctive characteristic of the viscous slowing down leading to glass formation: the emergence below some crossover temperature of a cooperative behaviour whose extension, however, remains limited to a mesoscopic length scale. Cooperativity is associated with the (collective) extension of the locally preferred structure whereas the limitation is a result of frustration. Glassiness is then self-generated as one decreases temperature.

Despite the absence of a well established minimal theoretical model of frustration in glass-forming liquids, progress has been made over the last decades in developing a statistical mechanical framework. Models have been built, based on such ideas as a coupling to a non-Abelian background, a uniform frustration, or a competition between effective interactions. Interestingly, several generic properties characterize such frustrated models, largely independently of their detailed structure. These properties are (1) avoided criticality, a genuine non-perturbative phenomenon induced by frustration, (2) the emergence of a complex free-energy landscape with an exponentially large number of ‘long-lived’ metastable states, and (3) the presence of topological defects.

The existence of the above three features opens the way to several theoretical routes to explain the phenomenology of glass-forming liquids within a frustration-based description.

The presence of a narrowly avoided critical point in the frustration–temperature diagram has been used to develop a phenomenological scaling analysis of supercooled liquids, the frustration-limited domain theory. The temperature associated with the avoided critical point marks a crossover between ‘ordinary’ liquid behaviour and ‘anomalous’ (cooperative, heterogeneous, super-Arrhenius) liquid behaviour, and fragility is predicted to be inversely related to frustration. Along a different line of thought, the emergence of a complex free-energy landscape is at the basis of the random first-order transition theory in which (super-Arrhenius) activated relaxation is associated with the configurational entropy resulting from the exponentially large number of metastable states. Finally, the existence of topological defects (primarily, line defects in three-dimensional geometrically frustrated media), which can form an entangled state and whose dynamics may be strongly constrained, is suggestive of a possible treatment by means of generalized kinetically constrained models. Whether or not these theoretical frameworks are compatible and which of them is the most efficient to describe the physics of glass formation are open questions.

The phenomenological scaling approach to the putative avoided critical point leads to a good qualitative and even, at the expense of course of introducing adjustable parameters, quantitative description of the salient phenomena in glass-forming liquids. However, its theoretical foundations, besides the property of avoided criticality, remain shaky. Support has been provided by computer simulation studies of Coulomb frustrated models, but no definite conclusion should be made. Needless to say that in spite of its appealing features and of the results derived so far much still remains to be done to make the frustration-based approach of supercooled liquids an operational, predictive, and microscopically founded theory of glass formation.

Acknowledgments

This work has been funded by the CNRS and the NSF. We would like to dedicate this article to Daniel Kivelson, whose stimulating presence and creative thinking we miss very much.

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