

Chapter 2

From Supercooled Liquids to RFOT

In the introductory chapter we focused on the supercooled and deeply supercooled branches in Fig. 1.1, as a way to properly introduce the phenomenon of the glassy slowdown, the fundamental notion of *metastable glassy state*, and lay the groundwork for the discussion of the Random First Order Theory of the glassy slowdown which this thesis is based upon.

This discussion takes place in the present chapter. We introduce the basics of RFOT, which posits that the slowdown of the dynamics in the glassy regime can be explained in terms of the insurgence of a great number of *metastable glassy states*, which trap the dynamics and hamper structural relaxation, thereby forcing the glass former in a metastable, out-of-equilibrium glass. We proceed by giving some arguments in support of the RFOT picture, in light of the phenomenology of the glassy slowdown discussed earlier. We then review summarily the RFOT picture over the course of a conceptual cooling experiment on a generic glass former, also discussing the possibility or necessity of an ideal glass transition. We conclude the chapter with a brief review of some other approaches to the glass problem.

2.1 The Random First Order Theory of the Glass Transition

The problem of formulating a theory of the glassy slowdown has been open for at least three decades, and by all appearances is still far from being solved. There are at least two reasons for this. The first one, of course, is that experiments, simulations and the like are very hard to perform because of the impossibly large experimental time which would be needed. As we said in the introduction, the theories of the glass transition which are in competition today were born as theories of supercooled liquids, and so their most relevant predictions, where with “relevant” we mean *predictions that could*

actually enable us to validate one theory and falsify the others, always kick in inside a deeply supercooled regime which is experimentally and numerically unreachable. A second reason, which is more subtle, is that it is not even very clear what a theory of glass transition is actually supposed to do. Since the main phenomenon is the glassy slowdown, a theory has at least to explain why the slowdown happens and propose a coherent theoretical picture for it. So it has, at the very least, to allow one to get back the VFT law, or some alternative law, like Bässler's, to fit the Angell's plot with. Already at this point we can see how fishy the situation is: there is not even agreement on which predictions the theory is supposed to produce; fits are just fits, after all. As a result of this, competition between the various theories is mainly based on criteria of theoretical consistency and predictive power [1], rather than quantitative, stringent tests that are impossible to perform and, even when they are performed, always leave some room for interpretation wherein incorrect theories could settle and thrive (the debate on the VFT law is a good, but definitely not the only, example).

If the aim of the theorist is to formulate a “universal” theory *à la Landau* (which is the declared goal and philosophy of RFOT, for example), then there is only one universal quantity that such a theory can be able to predict: namely, a critical exponent. Unfortunately, apart from the critical exponents of MCT [2] (which are anyway relative to a nonexistent dynamical arrest transition, as we are going to discuss), no such critical exponent has ever been measured, and indeed, since the glass transition is no transition at all, one even wonders where to look for such an exponent. As a matter of fact, the greatest, recent success of RFOT consisted in the prediction of the critical exponents of the jamming transition in hard spheres [3], the jamming transition [4–6] being a problem which initially was not related to glass forming liquids, if not in a tangential manner. The RFOT, as all other theories of the glass transition, was initially conceived as something that lives on the equilibrium, supercooled branch in Fig. 1.1. And yet it had to go all the way to $T = 0$ on the glassy branches (from a very pedestrian standpoint, the jamming transition is basically what happens to a large class of glasses when they are quenched down to zero temperature) to produce a quantitative, falsifiable prediction of an exponent. This strange fact can however teach us a lesson: theories on the glass transition *can* make falsifiable predictions, if only one bothers to look at the actual glass, which is the *only* thing we are actually

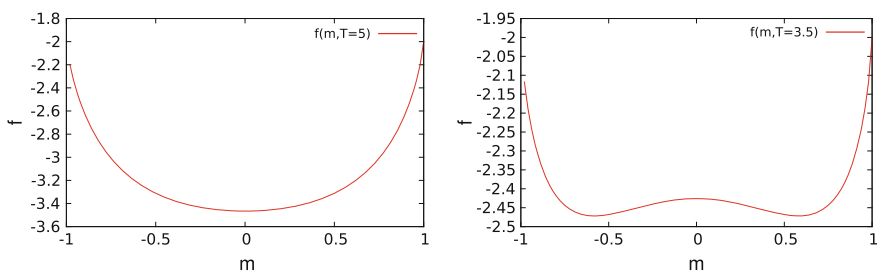


Fig. 2.1 Gibbs free energy as a function of the magnetization m for the ferromagnetic Curie-Weiss model above (left) and below (right) T_c

able to look at, and that we can experiment on. One of the aims of this thesis is to convince the reader that, even though RFOT struggles (as all other theories do), to affirm itself when it must describe supercooled liquids, it is definitely superior to (and has a lot more potential than) other theories when it comes to the treatment of the metastable glass. In the following we will explain RFOT with added focus on the central concept of metastable state, as a way to get this point across.

2.1.1 The Foundations of RFOT

The Random First Order Theory of the glass transition is based on three conceptual pillars:

1. The glassy slowdown is caused by the emergence, at low temperature, of a large collection of metastable states. The dynamics has to proceed as a series of activated barrier jumps between those states, causing the slowdown.
2. These states have a thermodynamic origin, in the sense that they can be identified with the minima of a static free-energy functional.
3. These states are exponentially many in the system size N , with their number given by $\mathcal{N} = e^{\Sigma N}$, where Σ is a static quantity called *configurational entropy* or *complexity*.

Summarizing, RFOT says that the slowdown of the relaxation dynamics of a liquid close to glassiness is due to the fact that it takes place in a very rough *free energy landscape* (FEL), characterized by the presence of an exponential number of minima. RFOT started essentially as a mean-field approach to the study of the free-energy landscape in generic disordered systems [1].

To fix ideas, let us consider the topical example, namely the Curie-Weiss theory of ferromagnetism. In that context, one is able to compute the Gibbs Free energy $f(m, T)$ of the system, as a function of the global magnetization m [7]. The Helmholtz free energy is the Legendre transform of the f , so it will be given, at zero external magnetic field, by the Gibbs free energy evaluated in its stationary points m^* , $f(m^*(T), T)$. At high temperature, only one minimum with zero magnetization is present and the system is paramagnetic and ergodic, i.e. it can visit all of the microscopic configurations that are allowed by conservation laws. But below a certain temperature T_c (see Fig. 2.1), the paramagnetic minimum splits in two distinct minima with $m^* \neq 0$, which correspond to two different *states* with opposite magnetizations. A phase transition takes place: in the thermodynamic limit, the system cannot go from one state to the other because it would have to surmount extensively ($\sim N$) large barriers to do so, and ergodicity is broken. From now on, the expressions “minimum of the energy landscape” and “metastable state” are to be considered interchangeable.

RFOT follows this basic nucleus, with only one (but very game-changing) modification. Since we are considering a disordered system, the Gibbs free energy gets replaced with a more complicated free energy functional which is a function of a

local order parameter, rather than a global one. In the case of spin systems, it will be a function of all the single-site magnetizations m_i and is referred to as Thouless-Anderson-Palmer (TAP) free energy [8]. In the case of liquids, it is usually a functional of the local density profile [9]. For a lattice gas we can for example define the Landau potential [1]

$$\Omega(\{\mu_i\}, T) \equiv -\frac{1}{\beta} \log \sum_{n_i} \exp \left[-\beta H(\{n_i\}) - \beta \sum_{i=1}^N n_i \mu_i \right], \quad (2.1)$$

where n_i is the site occupation number, H is the Hamiltonian and μ_i a local chemical potential. The free-energy functional $F(\{\rho_i\})$ will then be the Legendre transform of the Ω with respect to all the μ_i s:

$$F(\{\rho_i\}, T) = \Omega(\{\mu_i^*\}) + \sum_{i=1}^N \mu_i^* \rho_i, \quad (2.2)$$

with the μ_i^* s determined by the condition

$$\frac{\partial \Omega}{\partial \mu_i} + \rho_i = 0. \quad (2.3)$$

This definition can be generalized to the case of a density profile $\rho(\mathbf{x})$ in the continuum [7, 9], as we are going to see in the following. The FEL is the hyper-surface obtained by scanning the $F(\{\rho_i\})$ over all possible values of the local order parameters ρ_i .

Its stationary points, in particular, have cardinal importance. As the F is the Legendre transform of the Ω , this means that

$$\Omega(\{\mu_i = 0\}, T) = \min_{\{\rho_i\}} F(\{\rho_i\}, T), \quad (2.4)$$

which means that the thermodynamics of the system in absence of external chemical potentials is given by the free energy functional computed on its stationary points (as it happens if the Curie-Weiss model where the Helmholtz free energy is given by the Gibbs free energy computed in its stationary points in m).

With these definitions, the analogy with magnetic systems is clear: if we consider local density fluctuations

$$\delta \rho_i \equiv \rho_i - \rho, \quad (2.5)$$

where ρ is again the number density, we can see that the homogeneous, high temperature liquid ($\delta \rho_i = 0$) corresponds to the paramagnet, while the glass, with its amorphous nature, would correspond to a disordered ferromagnet with a rough free energy landscape. A crystal would not be homogeneous, but it would anyway have a periodic $\delta \rho_i$ profile, so it would be analogous to an anti-ferromagnet [7]. We can

appreciate how the idea of a glass as a system with a rough free energy landscape is indeed very reasonable (see for example [10–13]).

We now proceed to explain why the three tenets of RFOT are coherent with the phenomenology presented in the preceding chapter.

2.1.2 Dynamics: MCT and Goldstein's Picture

Let us start with points 1 and 2. Since those points make assertions about dynamics, we consider the theory that has been, up to very recently, the only first-principles theory for the dynamics of glass formers: the Mode Coupling Theory (MCT) [2, 14, 15].

2.1.2.1 Mode Coupling Theory and the p -spin

The aim of Mode Coupling Theory is to write a closed equation for the intermediate scattering function (or equivalently, the dynamical structure factor) $F_s(\mathbf{q}, t)$ for an equilibrated liquid close to glassiness. Let us consider the Newtonian (deterministic, without noise) dynamics of a generic liquid made of N particles with positions \mathbf{x}_i and momenta \mathbf{p}_i . Every macroscopic, time-dependent observable for such a system will be a function of the positions and momenta, $A(t) \equiv A(\{\mathbf{x}_i(t)\}, \{\mathbf{p}_i(t)\})$, like the density fluctuations in Eq. (1.15). From Hamilton's equations, one can derive the equation of motion for a generic observable $A(t)$

$$\frac{dA}{dt} = \{A(t), H\} \equiv i\mathcal{L}A(t), \quad (2.6)$$

where $\{A, B\}$ is the Poisson bracket

$$\{A, B\} = \sum_{i=1}^N \left(\frac{\partial A}{\partial \mathbf{x}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial B}{\partial \mathbf{x}_i} \cdot \frac{\partial A}{\partial \mathbf{p}_i} \right), \quad (2.7)$$

and we have defined the Liouville operator

$$\mathcal{L}(\bullet) \equiv -i\{\bullet, H\}. \quad (2.8)$$

We want to write an equation of motion for a correlator $C(t) \equiv \langle A(t)A(0) \rangle$, where $A(t) = \delta\rho_i(\mathbf{q}, t)$, and $\langle \bullet \rangle$ denotes an average over the initial conditions $\mathbf{x}_i(0)$ and $\mathbf{p}_i(0)$ carried out with the canonical distribution. The original derivation of MCT carries out this program using Zwanzig's projection operator formalism [16] (although field-theoretic derivations are available, see [17]). We skip directly to the final result

$$\frac{d^2 F(\mathbf{q}, t)}{dt^2} + \frac{\mathbf{q}^2 k_B T}{mS(q)} F(\mathbf{q}, t) + \frac{m}{Nk_B t} \int_0^t du \langle R_{-\mathbf{q}} R_{\mathbf{q}}(t) \rangle \frac{d}{dt} F(\mathbf{q}, t - u) = 0, \quad (2.9)$$

where

$$R_{\mathbf{q}}(t) = \frac{dJ_{\mathbf{q}}^L}{dt} - i \frac{i|\mathbf{q}|k_B T}{mS(\mathbf{q})} \delta\rho_{\mathbf{q}}.$$

and $J_{\mathbf{q}}^L$ is the longitudinal current [18]. This result is exact and does not require any simplifications. The nucleus of MCT consist in two uncontrolled approximations that are made on the memory kernel $\langle R_{-\mathbf{q}} R_{\mathbf{q}}(t) \rangle$ in order to get a closed, soluble equation. For the sake of brevity, we do not discuss them here and refer the interested reader to [18]. We just mention that the first step consists in projecting the kernel onto the space of bilinear density products, and the second in expressing the resulting four-point dynamical correlation function as a product of two two-point functions $F_s(\mathbf{q}, t)$ [1, 18]. At the end of the day, one gets for the memory kernel

$$\frac{m}{Nk_B t} \langle R_{-\mathbf{q}} R_{\mathbf{q}}(t) \rangle = \frac{\rho k_B T}{16\pi^3 m} \int d\mathbf{k} |\tilde{V}_{\mathbf{q}-\mathbf{k}, \mathbf{k}}|^2 F(k, t) F(|\mathbf{k} - \mathbf{q}|, t), \quad (2.10)$$

where the vertex $\tilde{V}_{\mathbf{q}-\mathbf{k}, \mathbf{k}}$ has the definition

$$\tilde{V}_{\mathbf{q}-\mathbf{k}, \mathbf{k}} \equiv \{(\hat{\mathbf{q}} \cdot \mathbf{k})c(|\mathbf{k}|) + \hat{\mathbf{q}} \cdot (\mathbf{q} - \mathbf{k})c(|\mathbf{q} - \mathbf{k}|)\}, \quad (2.11)$$

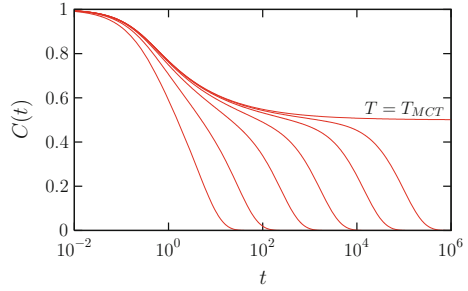
and $c(|\mathbf{q}|)$ is the direct correlation function [9]. With this expression, one can get a closed integro-differential equation for the intermediate scattering function, which can be solved easily once the static structure factor $S(\mathbf{q})$ is known. MCT is thus capable of predicting the relaxation patterns of glass formers from exclusive knowledge of static information. Despite the fact that the approximations involved are uncontrolled (which means that still today there is no idea as to what we are actually discarding in imposing them), this is anyway a remarkable result and MCT has enjoyed a lot of success since its inception.

The main prediction of MCT is undoubtedly the one of *dynamical arrest*: at high temperature the dynamical correlator decays exponentially to zero, as one would expect from the discussion in Sect. 1.2.3. However, at a certain temperature T_{MCT} (sometimes denoted simply as T_c), the correlator, after an initial fast relaxation, will remain stuck on a plateau and the system will never attain equilibrium: an ergodicity breaking takes place. At temperatures $T \gtrsim T_{MCT}$, one can observe a two-step decay reminiscent of the one discussed in Sect. 1.2.3 (see Fig. 2.2). In fact, the length of the plateau, which as we already know corresponds to the α -relaxation time, goes to infinity on approaching T_{MCT} as

$$\tau_{\alpha} \propto \frac{1}{(T - T_{MCT})^{\gamma}}, \quad (2.12)$$

where the γ exponent can be computed from the memory kernel. This sharp transition can be interpreted as one from liquid to solid, and since no information about a

Fig. 2.2 The various relaxation patterns predicted by MCT, on approaching from above the MCT transition. Reprinted figure with permission from Berthier and Biroli [1]. Copyright (2011) by the American Physical Society



crystalline state was used in the derivation, the solid the system freezes into must be non-crystalline, i.e., a *glass* [18].

This looks amazing: we have a first principles theory for the dynamics of glass formers which is able to predict the two-step relaxation patterns observed in simulations and experiments, and also predicts a sharp transition, with ergodicity breaking and divergence of the relaxation time, at a certain temperature. There is only one small problem, namely that, in pretty much all cases

$$T_{MCT} > T_g,$$

so one can easily go and see if the transition is actually there, and this is not the case: the α -relaxation time does grow sharply, but it stays finite and the system remains ergodic at temperatures below T_{MCT} . The MCT transition does not exist in real glass formers and must therefore be an artifact of the theory and its approximations [1, 19].

The reason for such a spectacular discrepancy would have been apparent some years after. Already in the original papers of Bengtzelius et al. [14] and Leutheusser [15], the authors proposed a “schematic” approximation of the MCT equation, which consisted in simplifying the wave vector dependence of the memory kernel, replacing the integral over \mathbf{k} with its value at a certain wave vector \mathbf{k}_0 where the static structure factor has a strong peak. With this simplification one gets the “schematic” MCT equation

$$\frac{d^2\phi(t)}{dt^2} + \Omega_0^2\phi(t) + \lambda \int_0^t du \phi^2(t-u)\dot{\phi}(u) = 0. \quad (2.13)$$

This equation happened to have the same form as the equation that would have been derived in [20] for the equilibrium dynamics for a certain class of schematic models of disordered ferromagnets, i.e. spin glasses (SG) [21]. The generic Hamiltonian for these models was first introduced in [22] and has the form

$$H = \sum_{i_1 < i_2 < \dots < i_p} J_{i_1, \dots, i_p} \sigma_{i_1} \sigma_{i_2} \dots \sigma_{i_p}, \quad (2.14)$$

where the couplings J_{i_1, \dots, i_p} are identically, independently distributed random variables (usually with a Gaussian probability distribution). They are called p -spin spherical models (PSMs) because of the p -body interaction involved (with $p > 2$), and because the spins are soft spins which must obey the spherical constraint

$$\sum_{i=1}^N \sigma_i^2 = N \quad (2.15)$$

Indeed, it was this analogy between MCT and the dynamics of p -spin SG that gave the original impulse for the formulation of RFOT as a theory for describing the glass transition [20, 23–26].

The PSM, although idealized and decidedly far from being a realistic model of a glass former, has numerous advantages: both its statics [27] and dynamics [28] can be exactly solved and the properties of its free-energy landscape can be studied in great detail. In particular, the presence, in a certain range of temperatures, of a great number of metastable minima with nonzero magnetization and free energy higher than the paramagnetic one (as postulated by RFOT) can be proven analytically [29] (see [30] for a review).

If one looks at the Hamiltonian (2.14), it can be seen immediately that all spins interact with one another: the model is *fully connected* and has no space structure, so it is a mean field (MF) model in the traditional sense. Because of this, the barriers between minima in the free-energy landscape scale as the system size N ; in the thermodynamic limit, N goes to infinity and barriers become in turn infinite: the system is unable to nucleate from one state to the other and remains forever stuck in the one it started from, producing an hard ergodicity breaking like the one observed in MCT [30].

This invites us to rationalize the ergodicity breaking predicted by MCT as a MF-born artifact: in the real world, barriers are always finite and the system can always escape from the state it is in, even though an extremely large time, of the order of τ_α , is needed to do so. Because of this, the glass former spends an extremely long time partially equilibrated inside a metastable state (and a plateau regime is consequently observed), but it eventually escapes and relaxes, restoring ergodicity and bringing back the supercooled liquid. But if we accept MCT to have a mean-field nature, because of the analogy with the dynamical equations for a MF model (where activated barrier crossing is forbidden by construction), then this activated scenario cannot take place: as soon as the system finds itself in a state, it cannot escape and ergodicity is broken. Today, the status of MCT as a mean-field theory of glassy dynamics, although not apparent from direct inspection of the MCT equations, is pretty much an accepted and established fact [1, 19]. Furthermore, the recent derivation of the dynamics of hard spheres in the limit of infinite spatial dimensions (which as we are going to see corresponds to the MF limit) [31] has shown that the *exact* dynamical equations do have an MCT-like form. We refer to [32, 33] for further reading on the MF nature of MCT.

2.1.2.2 Goldstein's Picture

As a matter of fact, the idea of the equilibrium dynamics of glass formers as a process dominated by activation was not very new even back then (even the exponential form of the $\tau_R(T)$ growth points towards this), as it had already been formulated by Goldstein [34] in 1969. Goldstein pictured the dynamics as taking place in the *potential energy landscape* (PEL) of the liquid, i.e. the hyper-surface obtained by scanning the interaction potential of the system over all values of particle coordinates. We can visualize it as a very rugged landscape of hills separated by narrow valleys [35], at the bottom of which lie the minima of the potential energy of the system, called *inherent structures* [19]. Adding thermal energy (i.e. raising the temperature) can be seen as a flooding of this landscape, with the level of the water higher the higher the temperature, and the system can be seen as a boat that has to navigate the landscape [35].

When the temperature is low, only a few, disconnected lakes of water are present, and to sail them all ergodically, the boat must be transported by land over the ridges that separate the lakes: this is an activation event, ruled by Arrhenius' law. Goldstein postulated that energy minima differed only by a change of a subextensive number n of degrees of freedom, and thus could be surmounted by a system equipped with a thermal energy of order $k_B T$. This way, the system as a whole (as described by a single point in configuration space) would always have been in the process of transition, but on the local level the jumps would have been separated by a timescale that would grow in temperature in an (at least) Arrhenius fashion as required by an activation-dominated mechanism. Thus Goldstein's picture provided a good explanation for the two-step relaxation observed in glass formers and for the exponential growth of the relaxation time: the short β -relaxation would correspond to our boat sailing inside a single lake on a short timescale, while the α -relaxation would correspond to a much longer transport by land of the boat, over a ridge and down into the next lake.

What happens if we keep flooding? Pictorially speaking, at a certain point the flood should become so severe that the water arrives at the level of the highest ridges which separate the valleys i.e. at the level of *saddles*, that is stationary points which have at least one unstable direction. When this happens, the boat only sees a large body of water wherein it is able to sail ergodically without the need for land transport: activation ceases to be the main mechanism of relaxation and Goldstein's scenario breaks down. This should happen for an high enough temperature T_x , and analogy with MCT suggest the identification

$$T_x \sim T_{MCT}$$

which has indeed been verified both in simulations [36] and experiments [37]. This identification bolsters the picture of glassy dynamics below T_{MCT} as an activation-dominated process.

The idea of the glass transition as a phenomenon ruled by a topological change in the energy landscape has indeed been very fruitful. In the PSM it can be proven analytically [38] that the stationary points of the energy landscape are minima (i.e.

they have no unstable directions) only up to a certain threshold energy E_{th} , above which saddles take over. It can be also seen that T_{MCT} corresponds to the temperature such that the typical stationary points visited by the system are exactly those with $E = E_{th}$, thereby providing an exact realization of Goldstein’s scenario. In real glass formers, analytic calculations of the sort are not possible and one must rely on numerics. Nevertheless, multiple studies (see for example [39–41] and the discussion in [19]) seem to confirm this picture. These results are very welcome, since they prove that even though in real liquids the MCT transition is wiped out by activation mechanisms, the topological transition is still present and fuels the fundamental analogy with the PSM even for out of MF glass formers.

Since the MCT temperature is the one where a crossover to activated dynamics takes place, and metastable states responsible for the slowdown appear, it is commonly taken as the reference temperature where the onset of “glassiness” is located, also because it has a fundamental and unambiguous definition, contrary to T_g . From now on, when we say “low temperature”, we mean that we are below T_{MCT} .

There is however an important warning to give: potential energy landscapes and free energy landscapes are not the same thing and one must not confuse the two: the energy landscape is defined in the configuration space of the liquid and is independent of the temperature, while the free energy landscape is defined in the space of local order parameters and changes when the temperature is varied. Of course the two are the same when $T = 0$, and it could make sense to keep the identification as long as the temperature is very low, but attention must always be paid and the idea of identifying states with minima in the potential energy landscape is just plain wrong [1, 19, 42].

At the end of this paragraph, we hope that the reader is convinced that the two-step relaxation observed in glass formers is reasonably interpreted as originated by the appearance, in the free energy landscape of the system, of a collection of metastable minima (states) which exert a trapping effect on the dynamics for a stretch of time $t \simeq \tau_\alpha$ and keep the liquid from attaining relaxation and flowing. And that the identification of these states with minima of the free energy landscape appears reasonable in light of the analogy between MCT and the dynamics of the PSM, and by the presence of a topological transition in the PEL in both cases. Summarizing, we hope that he now believes that the two first tenets of RFOT appear at least a reasonable starting point for a theory of the glass transition.

2.1.3 Complexity: Kauzmann’s Paradox

Let us now turn to point 3. We have to ask ourselves the question “how many states can one have?”

How can we label a state? As we said, a state is a minimum of the FEL identified by a set $\{\rho_i^*\}$ of local densities (in liquids), or a set $\{m_i^*\}$ of local magnetizations (in spin models). Thus a glassy state in a realistic glass former corresponds to an amorphous density profile the liquid is frozen into. We had already encountered

this picture when discussing caging: particles can only vibrate around equilibrium positions arranged in an amorphous structure, thus every state corresponds to such a structure.

Since these structures are amorphous, we can already surmise that a lot of them should exist. There are not many ways of arranging particles in an ordered structure, but there sure are a lot of possible disordered arrangements. Intuitively, the number of such arrangements should be equal to the number of configurations the liquid has at its disposal, divided by the number of configurations visited by the glass during the vibration around the amorphous structure.

The thermodynamic potential that logarithmically counts the configurations available to the system is the entropy, and we already know from the discussion in Sect. 1.2.4 that the vibrational excitations of particles in a glass are not too different from the ones found in crystals. We could thus hope to count the number of amorphous structures by taking the supercooled liquid entropy and subtracting from it the entropy of the corresponding crystal, as a reasonable proxy for the vibrational entropy of the glass.¹ This leads to the definition of the *excess entropy*

$$S_{exc}(t) \equiv S_{liq}(T) - S_{cr}(T), \quad (2.16)$$

which we can measure by exploiting the relation between entropy and specific heat [19]

$$\frac{dS}{dT} = \frac{c_p(T)}{T}. \quad (2.17)$$

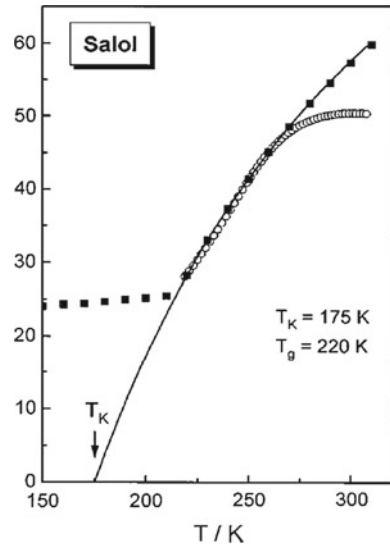
In Fig. 2.3 we show the excess entropy as a function of the temperature for salol, a fragile glass former. We can see that the excess entropy freezes at T_g to the value it had in the supercooled liquid: this is due to the fact that there is no latent heat at the glass transition (differently from what happens at the melting point T_m , see Fig. 1.1), so the entropy is continuous at T_g . On further cooling, the excess entropy stays pretty much constant. This is of no surprise, as its derivative is proportional to the difference between liquid and crystalline specific heat, and we already mentioned in Sect. 1.2.4 that $c_p^{liq} \simeq c_p^{cr}$. Nevertheless, the excess entropy at T_g is of the order of $3k_B$ per molecule, which is large [44]: the number \mathcal{N} of possible amorphous configurations scales exponentially with the size of the system

$$\mathcal{N} \simeq e^{\Sigma N} \quad (2.18)$$

where Σ is the *complexity* (some prefer to call it *configurational entropy* and denote it S_c or s_c , but it is a matter of taste), and is the central static quantity of RFOT.

¹A justification is that vibrational contributions are given by an harmonic expansion around a potential energy minimum, and the fact that the minimum corresponds to an ordered (crystal) or disordered (glass) arrangement of the particles should not change matters much. This is reasonable, but it does not make sense for systems where a harmonic expansion does not exist, like hard spheres [19].

Fig. 2.3 Excess entropy as a function of temperature for salol, in $\text{kJ}/(\text{K} \times \text{mol})$. Dots are experimental data, while the line is a fit of the form $S_{\text{exc}}(T) = A(1 - T_K/T)$. Reprinted from Richert and Angell [43] with the permission of AIP Publishing



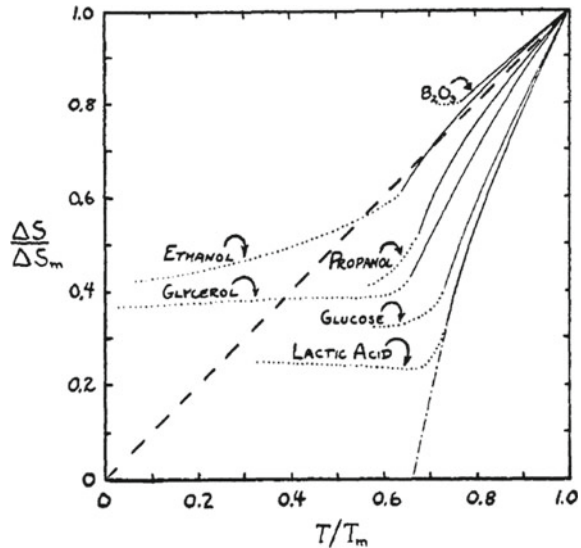
In glass formers, the presence of an exponentially large number of metastable glassy states (and thus the possibility to define a configurational entropy) is a reasonable hypothesis (at least we hope that this discussion made it easier to accept), but it is an incontrovertible fact in the PSM, where the complexity can be analytically computed [29, 30] starting directly from the stationary points of the TAP free energy [8]. Again the PSM furnishes us with a setting wherein the basic ideas of RFOT are exactly realized.

2.1.3.1 Kauzmann's Entropy Crisis

If we look closely at Fig. 2.3, we can see a curious thing. The extrapolation of the excess entropy to temperatures below T_g goes to zero at about 175 K, a value far above absolute zero. So there is a finite temperature where the entropy of the supercooled liquid would become equal to that of the crystal, a very counter-intuitive phenomenon. We would expect the liquid entropy to be always above the crystalline one (a liquid is disordered, a crystal is not) for any finite temperature.

This vanishing of the excess entropy for finite temperature had indeed been known for quite some time, as it was first described by Kauzmann in 1948 [45]. What Kauzmann did was to extrapolate below T_g the data for various observables (enthalpy, free volume, energy, etc.), including the excess entropy. From Fig. 2.4, we can observe that the excess entropy seems to vanish for temperature different from zero in various glass formers. This temperature has been christened T_K in honor of Kauzmann, and the vanishing of the excess entropy is referred to as *Kauzmann's paradox*, or *Kauzmann's entropy crisis*.

Fig. 2.4 The original figure from Kauzmann's paper. For various glass formers, the temperature seems to vanish at $T = T_K$, $T_K \neq 0$. Reprinted from [19]



We must immediately state a fact: Kauzmann's paradox was a paradox only back then. As strange as the vanishing of the excess entropy can appear, there is no law of nature that actually forbids it. The crystallization transition in hard spheres for example is precisely due to the fact that the crystalline entropy becomes larger than the liquid one at high enough density [46], so nowadays we know that the entropy crisis does not violate any fundamental laws and its presence is not a serious problem. Nevertheless, it appeared paradoxical back then, and Kauzmann himself, in his paper, was eager to find a way out of it.

There are two possible interpretations. If we believe the fact that the excess entropy is a proxy for the configurational entropy Σ , and that it is possible, at least in principle, to equilibrate the supercooled liquid down to T_K , then a phase transition must be located there. If the configurational entropy vanishes linearly at T_K as Fig. 2.4 suggests, then the corresponding specific heat has a step at T_K , signature of a second-order transition [1]. This transition has been dubbed the *ideal glass transition* (sometimes *Kauzmann transition*).

Kauzmann himself did not believe this, and he proposed an alternative argument: it is not possible to equilibrate the supercooled liquid down to T_K , because the relaxation time grows so much that, in the end, it becomes larger than the crystal nucleation time. So either the glass former goes out of equilibrium and forms a glass, or nucleation will kick in and crystallize our sample. In any case, the supercooled liquid ceases to exist and the paradox at T_K is avoided. We refer to [19] for a discussion on this point.

2.1.3.2 Is the Ideal Glass Transition Necessary?

Unsurprisingly, the interpretation of T_K as the locus of a phase transition had a lot more fortune. The idea that the glassy slowdown is a manifestation of an underlying critical point at T_K is indeed very appealing and conceptually elegant. It also brings back the glass problem to a context, the one of critical phenomena, that physicists are very familiar with, and for which a lot of theoretical tools are at their disposal.

An argument in favor of this idea is that the temperature T_K is always very near to the temperature T_0 where the VFT fit has a divergence, and this applies to glass formers which have T_g s that vary from 50 to 1000 K (see [47] for a compilation of data and [48] for a discussion). The coincidence is indeed remarkable, so much that for many proponents of RFOT, it cannot be a coincidence and they see it as incontrovertible proof that the ideal glass transition exists. However, there are glass formers where T_K and T_0 can differ as much as 20% [49], so such unshakable certainty is ill-advised, at least for now.

The idea of an ideal glass transition at T_K is indeed so powerful and fascinating, that over the years it has come to be identified as the main prediction of RFOT. This is so much true, that most research articles that go and try to disprove RFOT focus on disproving the existence of the ideal glass transition (see for example [50, 51]). This misunderstanding is also probably due to the fact that most models used in RFOT theory do have an ideal glass transition, starting from the paradigmatic PSM [30].

We argue here that identifying the ideal glass transition (and also the VFT law) with RFOT means missing the point: none of the three tenets that we formulated at the beginning of this section has anything to do with the ideal glass transition. For the RFOT picture to hold, we only need that the insurgence of metastable states cause the glassy slowdown, and that those metastable states have a *static* origin in the sense that they can be identified with the minima of a suitable free energy functional. This scenario can unfold independently from the presence or not of an ideal glass transition at finite temperature.

In summary, we argue that even an avoided transition ($T_K = 0$) is good enough for RFOT [1].

2.1.4 Summary of RFOT: For T_{MCT} to T_K

In the preceding sections we have provided enough (at least we hope) arguments to convince the reader that the RFOT theory of the glass transition is a good starting point for a description of the physics of glass formers. Let us now give a more unified perspective, and summarize what happens during a cooling experiment of a glass former according to RFOT.

To be completely general, we focus on a generic system whose micro-configurations are denoted as \mathcal{C} and has a Hamiltonian $H(\mathcal{C})$. The partition function is

$$Z = \int d\mathcal{C} e^{-\beta H(\mathcal{C})}. \quad (2.19)$$

From the discussion of Sect. 1.2.4 we know that states can be visualized as “patches” of configurations, namely those configurations which are visited by the system as particles vibrate around the amorphous structure that identifies the state. Assuming that each configuration can be unambiguously assigned to a single state, and that the “tiling” so generated covers the whole space of configurations,² we can write the partition function as

$$Z = \sum_{\alpha} \int_{\mathcal{C} \in \alpha} d\mathcal{C} e^{-\beta H(\mathcal{C})} = \sum_{\alpha} e^{-\beta N f_{\alpha}}. \quad (2.20)$$

Where α is an index that identifies a state, and we have defined the intensive free energy f_{α} of a state. We can transform the sum over α in an integral using Dirac delta functions

$$\sum_{\alpha} e^{-\beta N f_{\alpha}} = \int df \sum_{\alpha} \delta(f - f_{\alpha}) e^{-\beta N f}. \quad (2.21)$$

We now notice that

$$\sum_{\alpha} \delta(f - f_{\alpha}) = \mathcal{N}(f) = e^{N \Sigma(f, \beta)}, \quad (2.22)$$

so that we are able to easily introduce the f -dependent complexity, which logarithmically counts the number of states with have the same in-state free energy f , or equivalently, the number of minima in the FEL who have the same height f . We get

$$Z = \int df e^{-\beta N [f - T \Sigma(f, \beta)]}. \quad (2.23)$$

In the thermodynamic limit, we can evaluate this integral with the saddle-point (or steepest-descent) method [53], getting

$$Z = e^{-\beta N [f^* - T \Sigma(f^*, \beta)]}, \quad (2.24)$$

where f^* is determined by the condition

$$\frac{d\Sigma}{df} = \frac{1}{T}, \quad (2.25)$$

which means that the partition function is dominated by the states with $f = f^*$ only, while the others do not have any impact on the thermodynamics of the system. The states with $f = f^*$ are referred to as *equilibrium states* for this reason, and the complexity of those states

²This is a very strong assumption, but it can be rigorously proven to be true in the PSM, see [52].

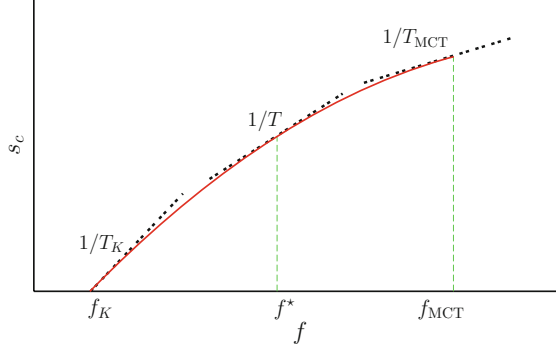


Fig. 2.5 The typical form of the complexity as a function of the in-state free energy f . It is a monotonically increasing function in an interval $[f_{min}, f_{MCT}]$, and zero otherwise. For $f > f_{MCT}$, the FEL is dominated by unstable stationary points and the complexity is accordingly zero, as it happens in the PEL for $E > E_{th}$. At f_{MCT} stable minima, which can be found everywhere in the interval $[f_{min}, f_{MCT}]$, start to appear. At f_{min} , the complexity vanishes continuously as the number of minima becomes sub-exponential. The states with $f = f_{min}$ and those with $f = f_{MCT}$ correspond to the typical equilibrium states visited by the system at $T = T_K$ and $T = T_{MCT}$ respectively. Reprinted figure with permission from Berthier and Biroli [1]. Copyright (2011) by the American Physical Society

$$\Sigma(f^*(\beta), \beta) \equiv \Sigma(\beta), \quad (2.26)$$

is accordingly called the *equilibrium complexity*, the one that is measured in experiments and simulations.

The typical form of the complexity for a system with an RFOT-like FEL is shown in Fig. 2.5. Let us now perform an infinitely slow cooling (such that the system is always equilibrated) and discuss the various regimes that take place as the system scans different regions of the FEL while $f^*(T)$ changes with temperature.

- $T > T_{MCT}$: At high temperature, the minimization of the the free energy functional yields only the homogeneous solution $\rho_i^* = \rho \forall i$, with the corresponding free-energy $F(\{\rho\}) = F_{liq}$. The system is ergodic and liquid.
- $T_K < T < T_{MCT}$: At $T = T_{MCT}$, $f^* = f_{MCT}$, states start to have an impact on the system and the relaxation time starts to increase. Those states are metastable since $f^* > F_{liq}$, but one can see that $F = f^* - T\Sigma(f^*, T) = F_{liq}(T)$ for every T in this interval, and that the free energy is analytic at T_{MCT} .

This can be interpreted as follows: for $T_K < T < T_{MCT}$, the equilibrium liquid splits up in a collection of states, each identified by an amorphous structure and a set of vibration modes around it. On timescales $\tau_\beta < t < \tau_\alpha$, the system remains trapped in one of the equilibrium states with $f = f^*$, producing the plateau regime observed in the dynamics. When at $t \simeq \tau_\alpha$ relaxation approaches, the system starts to visit the other equilibrium glassy states gaining an entropic advantage in the form of $-T\Sigma(f^*, T)$, bringing back the supercooled liquid with its free energy $F_{liq}(T) = f^* - T\Sigma(f^*, T)$. This way, although states appear at T_{MCT} , they only

impact the dynamics of the system and its equilibrium state remains always the supercooled liquid (as experimentally observed). In fact, if we compute the probability, at equilibrium, to find the system in one particular equilibrium state α , we get

$$P_\alpha = \frac{\int_{\mathcal{C} \in \alpha} d\mathcal{C} e^{-\beta H(\mathcal{C})}}{\int d\mathcal{C} e^{-\beta H(\mathcal{C})}} = \frac{e^{-\beta N f^*}}{e^{-\beta N (f^* - T \Sigma(f^*))}} = e^{-N \Sigma(f^*)} \xrightarrow{N \rightarrow \infty} 0, \quad (2.27)$$

so the system “hops” seamlessly between all possible equilibrium states.

On lowering T , f^* will decrease and the system will sample states in lower and lower regions of the energy landscape. We stress the fact that such a protocol is very difficult to realize in practice as the relaxation time starts to grow sharply below T_{MCT} . If one performs an infinitely rapid quenching dynamics (like the MCT one), the system will not have time to descend in the FEL and will remain stuck in the highest states with maximal complexity.

Of course, an hopping process like the one we described can take place only in real systems. In MF models, once the system is blocked in a state, it can never get out, as MCT predicts.

- **$T \leq T_K$** At $T = T_K$, the equilibrium states become the ones with $f = f_{min}$ and the complexity vanishes. We have still $f_{min} - T \Sigma(f_{min}) = F_{liq}$, and the total entropy $\Sigma + s_{vib}$ is continuous, but the specific heat ($c_p = \frac{dS}{d \log T}$) has a jump induced by the vanishing of Σ : the entropy vanishing scenario of Kauzmann is realized and the ideal glass transition takes place.

Below T_K , the number of states becomes sub-exponential and the system can now be found, at equilibrium, inside a single glassy state, thus yielding a stable, thermodynamic glass.

This is how the glassy slowdown happens according to RFOT. One must admit that the picture is quite elegant and brings together nicely many different inputs and observations, from MCT to excess entropy to Kauzmann’s paradox. Needless to say, the PSM realizes this scenario exactly [30].

2.1.5 Beyond Mean Field: Scaling and the Mosaic

We mentioned at the start of this section that a theory of the glass transition has at least to describe well the glassy slowdown, which means that it has to reproduce the VFT fit (or some other fit) of the τ_R versus T dependence. Within RFOT, this means that we need to compute τ_α as a function of T , and to do so, we must focus on the dynamics, in particular on long timescales comparable with τ_α , when relaxation occurs.

But this brings to the surface the great weakness of RFOT [1], namely its reliance over the concept of metastable state, and consequently on a mean-field description. The MF nature of RFOT models (starting from the PSM, but there are many others)

makes it, on one side, an ideal playground to study metastability: states are sharply defined, they have an infinite lifetime, and their properties can be studied analytically even for realistic models of glass formers as we are going to see in the following of this thesis. But on the other side, the failure to take into account activation mechanisms and non-MF effects in general, means that the theory is found wanting when attempting to describe the regime wherein non-MF effects come into play, which is also the regime wherein relaxation occurs (remember the wrong MCT prediction of a transition at T_{MCT}). This difficulty in going beyond MF (see for example [54] for a dynamics-based attempt) is the great weakness of RFOT and a solution to this problem does not seem to be forthcoming [1]. As a result of this, the connection between RFOT and the dynamics of the system on long ($t \simeq \tau_\alpha$) timescales comes from a bundle of phenomenological scaling arguments, which goes under the name of *mosaic theory* [24, 26, 44, 55], and was essentially conceived as a reworking of the old Adam-Gibbs theory [56] to include the notion of complexity.

Mosaic theory is an attempt to bring out of MF the MF-based concept of metastable state: in the real world, the τ_α timescale is always finite, so the concept of metastable state must become local in time. Indeed, since metastable states are, well, metastable, they are intrinsically out-of-equilibrium objects and so any attempt at a rigorous definition must start from the dynamics (see for example [57, 58]). Another problem comes from the fact that states, being MF objects, do not take into account at all the notion of *real space*. In MF models, there is no space structure, so it makes sense to talk about the system globally being in a “state” and hopping to another global state at the onset of relaxation as we said in the preceding paragraph. Once real space comes into play, this picture clearly makes no sense: hopping from one state to another takes place through a nucleation mechanism which can only be *local* in space: as soon as a sufficient time passes for activation to happen, droplets will start to form at certain points in the sample, and each of them will be in a certain “state”. There is absolutely no reason for them to be all in the same state, since all states with $f = f^*$ (including the one the system is about to leave) have the same free energy and thus they are completely degenerate. Indeed, if there were a free energy gain in passing from one state to another, it would mean that the system is not at equilibrium, in contrast to the RFOT picture which asserts that the equilibrated, liquid system is restored by the seamless hopping process between states. Thus, we can expect that the original state will break up in a collection of tiles (a mosaic), each of them in a different state. The fact that rearrangements must be local should not come as a surprise, considering that the local nature of rearrangements in glass formers had been already pointed out by Goldstein [34]. In summary, states must be defined locally both in space and time, i.e. they are characterized both by a *timescale* τ_α and a *lengthscale* ξ .

We are interested in computing the timescale as a proxy for τ_R . What we can do is work out the lengthscale, get from it an estimate of the barrier size to rearrangement, and get from it the timescale using Arrhenius’ formula. Since we have said that rearrangement should take place through nucleation, let us assume that our glass former is in a state γ . When a time $t \simeq \tau_\alpha$ has passed, thermal fluctuations will form a droplet of linear size R , typically in another state δ . On the boundary, the mismatch between the two states will induce a free energy *cost* in the form of a surface tension

$$\Upsilon R^\theta, \quad (2.28)$$

where θ is a generic exponent, $\theta \leq d - 1$. Usually it is equal to $d - 1$ (where d is the dimension of space) since it represents a surface term, but this need not be the case in general [19]. This free energy price has to be balanced by a free energy *gain* of some sort. In nucleation theory it is usually given by the free energy difference between the two coexisting phases, but in this case the two states have the same free energy $f = f^*$. Thus the complexity comes into play: the droplet can be found in $\mathcal{N} = e^{R^d \Sigma(T)}$ different states, so it is of course invited to explore them all and gain an entropic advantage in the form of $-T \Sigma(T) R^d$ rather than staying in state γ . The total energy barrier for forming the droplet is

$$\Delta F = \Upsilon R^\theta - T \Sigma(T) R^d, \quad (2.29)$$

which means that large droplets will tend to survive, while small ones will tend to go back to the background state. The crossover between the two happens at a lengthscale ξ which can be obtained by setting ΔF to zero. We get:

$$\xi = \left(\frac{\Upsilon}{T \Sigma(T)} \right)^{\frac{1}{d-\theta}}. \quad (2.30)$$

Now, following [26], we fix the barrier height Δ as

$$\Delta \equiv \max_R \Delta F(R) = \frac{\Upsilon^{\frac{d}{d-\theta}}}{[T \Sigma(T)]^{\frac{\theta}{d-\theta}}}, \quad (2.31)$$

and using Arrhenius' formula we get

$$\tau_R = \tau_0 \exp \left(\frac{\Upsilon^{\frac{d}{d-\theta}}}{k_B T [T \Sigma(T)]^{\frac{\theta}{d-\theta}}} \right). \quad (2.32)$$

Now we know that near to T_K

$$\Sigma(T) \simeq A(T - T_K), \quad (2.33)$$

so we can plug this into the formula for τ_R , getting

$$\tau_R = \tau_0 \exp \left(\frac{\Upsilon^{\frac{d}{d-\theta}}}{k_B T [A T (T - T_K)]^{\frac{\theta}{d-\theta}}} \right), \quad (2.34)$$

so we get a law which looks like the VFT one, although not the same. However, in [26] it was claimed that $\theta = d/2$, which would give for τ_R

$$\tau_R = \tau_0 \exp\left(\frac{\Upsilon^2}{k_B T [AT(T - T_K)]}\right) \underset{T \rightarrow T_K}{\simeq} \tau_0 \exp\left(\frac{B}{T - T_K}\right), \quad (2.35)$$

exactly the VFT law. We must however state again that the VFT law is just a fit, not a fundamental law or the result of a first-principles computation, so perhaps it is not worth it to fiddle with θ and make assumptions about its value just for the sake of getting it back. Using the (2.34) with θ as a fitting parameter would probably do an even better job than the VFT and there are alternative laws which provide anyway a good fit of the data.

Summarizing, even if we had to use some arguments (and some common sense) to get the results, RFOT indeed passes the test, in the sense that it does provide a good explanation for the super-Arrhenius increase of τ_R , in the form of the *complexity*: the barrier size scales with the inverse of a power of Σ and thus increases when T_K is approached, causing a sharper increase than the simple Arrhenius' one (where the barrier would be constant).

There is an alternative formulation of the mosaic theory which does not use nucleation and is conceptually more robust than the one we just presented, we refer to [19, 59] for details. In [59], the authors also propose a method to measure the lengthscale ξ , through the definition of a special correlation function, the *point-to-set* correlation function. The measurement of ξ using this tool has indeed given encouraging results and a growth of ξ on supercooling is observed [60], so the mosaic picture, and RFOT with it, does seem to be on the right track when it comes to the description of supercooled liquids. We refer to [19] for an in-depth discussion on the point-to-set lengthscale.

We conclude here our exposition of RFOT, and we hope that we managed to make it look at least as a reasonable starting point for a theory of glasses. For further reading, we refer to [19] for a pedagogical approach, to [1] for a more technical point of view, and to [44] for a critical assessment. We refer also the reviews [55, 61], and a book [62].

2.2 Other Approaches

A much beloved quote by prof. D. Weitz says “There are more theories of the glass transition than there are theorists who propose them”. While it is certain that prof. Weitz was a little exaggerating, it is true that there are indeed many different theoretical pictures for the glassy slowdown. This is not necessarily a bad thing, since it shows that this field of research has still many open problems, there is still a lot of work to do, and the debate is fluid and lively (tellingly, prof. Weitz's quote is much beloved by glass theorists themselves), so there is no shortage of “other approaches” that we could talk about.

However, since they are so many, we will focus here only on the ones that are most popular at the moment, and that are more suitable of an analytic, statistical-

mechanical treatment. Reviews on the approaches we will leave out can be found for example at [63–65], and we refer to section IV.A of [1] for more references.

2.2.1 Dynamic Facilitation Theory

The Dynamic Facilitation Theory (DFT) [66–68] picture is in many ways completely specular to the RFOT approach. Whereas RFOT posits a static explanation (in the form of metastable states) for the glassy slowdown, DFT favors a completely dynamical approach and postulates that thermodynamics plays absolutely no role. While RFOT relies mainly on MF-born concepts (like global metastable states and the FEL) and on MF models, DFT is firmly rooted in real space and its paradigmatic models all are finite-dimensional. While RFOT is at pain when it comes to link its thermodynamic foundations to dynamics, in DFT dynamics is the very cornerstone of the approach.

These stark differences between the two approaches come from their differing views about what is the distinguishing phenomenological fingerprint of glassiness. For RFOT, the fingerprint of glassiness is activation, *à la Goldstein*, so RFOT naturally stages itself into the FEL, and as a result of this it naturally relies on a static MF description of the FEL. According to DFT, the fingerprint is *cooperativity*, which takes place during the dynamics of the system when viewed in real space. So DFT, accordingly, stages itself in real space and naturally relies on dynamical tools [19].

The philosophy of DFT is that diffusion and relaxation can only be achieved through cooperativity: for a particle to escape its cage, all particles around it must also decay and move away, and this in turn will stimulate other particles to move [69]. So, we can see decaging process as the creation of a new *defect* (a cluster of mobile particles), which is in turn susceptible of inducing (*facilitating*) mobility in nearby regions, creating other defects. This picture is undoubtedly reasonable, as we have seen in paragraph Sect. 1.2.5 that facilitation does play a role in the dynamics of glass formers close to T_g . It looks even more reasonable in light of the fact that it is possible to define models based exclusively on the idea of dynamic facilitation, called Kinetically Constrained Models (KCMs) [67].

2.2.1.1 Kinetically Constrained Models

KCMs can come in different flavors, but they all have two things in common: their thermodynamics is trivial, and their dynamics is constrained by rules which mimic the facilitation picture. A first example is the Kob-Andersen (KA) lattice gas [70], wherein a particle can hop from one site to the other only if i) it is empty, and ii) if there are less than m neighbors around it ($m = 6$ on a cubic lattice would correspond to the unconstrained gas). It is basically a model that enforces the notion of caging in a strict sense, and can be studied for various values of m and different lattice topologies, from cubic to Bethe [67].

Another champion of KCMs is the Fredricksen-Andersen (FA) model [71], which opts for a specular philosophy to the one of the KA model, focusing on holes rather than particles. Each site on the lattice can be mobile $n_i = 1$ or not $n_i = 0$. The Hamiltonian, again, contains no interaction

$$H_{FA} = J \sum_i n_i \quad (2.36)$$

and $\langle n_i \rangle \propto \exp(-\beta J)$, so that mobility is suppressed at low temperatures (as one would expect). The dynamics, for its part, takes place with the usual Glauber rules, but a site can make a transition from mobile to non-mobile only if there are at least other k neighboring mobile sites. A variation on the FA is the East model [72], where only sites on the left in each space dimension can facilitate the dynamics.

2.2.1.2 Strengths and Weaknesses

The main advantage of DFT lies in the fact that dynamics is the very core of the approach, so, for example, their predictions on the relaxation time can be easily obtained. Some models show a strong, Arrhenius-like behavior, like the FA with $k = 1$, while others have a more fragile character. The East model for example has $\log \tau_\alpha \simeq \frac{1}{T^2}$, which quite reminisces Bässler's law, Eq. (1.7), and the FA on a square lattice with $k = 2$ (the original version of the model from [71]) is even more fragile, with $\tau_\alpha \simeq \exp[\exp(c/T)]$. The great majority of KCMs do not predict a divergence of the relaxation time at finite temperature, but it is possible to define a KCM in such a way that a divergence is present [73]. Despite this, their predictions for τ_α can be shown to fit experimental viscosity data quite well, see for example [74, 75]. So DFT does pass the test, perhaps in an even more convincing manner than RFOT.

Another great advantage of KCMs lies in the fact that they naturally reproduce the phenomenon of dynamical heterogeneities [76, 77], so much that some studies on dynamical heterogeneities were actually motivated by their observation in the context of KCMs. They also give the possibility to study in great detail multi-point correlation functions (like the G_4), even enabling researchers to get rigorous scaling relations between susceptibilities, lengthscales and timescales [78, 79]. The DFT picture provides also a natural explanation of the violation of the Stokes-Einstein relation for viscosity and diffusion [80]. We stress that all these predictions come easily from DFT, while a dynamics-based formulation of RFOT is still lacking (see [31] for a possible starting point), so there is no denying that the DFT picture is clearly superior to RFOT when it comes to the study of dynamics in the supercooled liquid regime.

However, there are some weaknesses. The biggest, conceptual weakness lies in the exclusive role attributed to facilitation, which is seen as the *only* possible mechanism for relaxation. To make this more clear, this means that mobility and defects cannot be created in any way: a region of the system which is not mobile cannot relax

unless a drifting defect visits it, and no spontaneous motion is possible (mobility is conserved). This is a very strong assumption, which may not be true, see for example [81].

On the other hand KCMs cannot make do without the assumption of mobility conservation, or at least without assuming that violations to this assumption become more and more rare when T is lowered. If mobility can be created and destroyed, KCMs immediately become trivial models and their glassy phenomenology is wiped out [1], which is a huge and undefended weak point.

In addition to this, as much as RFOT suffers from an over-reliance on MF-based statics, DFT seems to suffer from an over-reliance on dynamics. In particular, the fact that KCMs all have a trivial thermodynamics does not even seem a necessity, and it constitutes no proof that glass formers share this feature. Moreover, there is a subtle point, namely the fact that having a trivial thermodynamics does not mean that all the RFOT based phenomenology of metastable states cannot take place in KCMs. The thermodynamics of RFOT models is indeed trivial, in a way, since from T_{MCT} down to T_K equilibrium is always given by the supercooled liquid; and indeed, the presence of metastable states cannot be detected using standard statistical mechanical tools, requiring to use of the TAP approach [8] or the replica method [7]. In summary, we argue that the triviality of the standard thermodynamics of KCMs does not imply the triviality of their replica-based (or state-following based) thermodynamics.

A less severe and more taste-related weakness is the one of predictive power. Intuitively, for a theory to be very predictive we should have to put a few things into it, and get a lot in return. DFT, as we just detailed, does give you a lot, but it also requires you to put a lot inside. As interesting as KCMs are, there is at present no way of linking them to microscopic models of glass formers [1]. Their dynamical rules in particular are just imposed from the outside without any microscopic or first-principles justification, and they cannot be generally derived (see [82] for an exception) from an interaction Hamiltonian.

This means that in order to get quantitative predictions about real glass formers, KCMs must usually be suitably “tuned” using experimental or numerical data, which is unpleasant. We will return to this point in the following when discussing the DFT approach to metastable glasses. We will see that, while DFT needs extensive tuning to work well, the RFOT-based state following construction enables us to get predictions from first principles, at the only price of an Hamiltonian.

2.2.2 Frustration Limited Domains

According to the Frustration Limited Domains (FLD) [83] picture, the fingerprint of glassiness is disorder and the amorphous nature of the glass phase, which is rationalized as a consequence of geometric frustration. Frustration can be broadly defined as the incompatibility between a *locally* preferred arrangement, and the symmetry of the space it finds itself in, thereby rendering the local structure incapable of tiling the whole space forming a global periodic structure.

A pedagogical example is a triangle of spins with anti-ferromagnetic interactions: the local preferred structure would be a $+1$ spin and a -1 spin at the end of each bond, but the triangular topology renders this arrangement impossible: at least one bond is not satisfied (which means that the relative energy cannot be minimized), and as a result there are three possible (and equivalent) optimum frustrated arrangements. This example illustrates how the frustration is caused by geometry: on a square lattice, there would have been no problem. Moreover, it also illustrates how frustration is also a source of degeneracy and multiplicity, an important ingredient in the context of amorphous materials. This ideas can also apply to particle systems. It is for example known that the local preferred order for packings of spheres in $d = 3$ is the icosahedral one, which is however incompatible with periodic ordering [84].

According to FLD, the glassy slowdown is a manifestation of a second-order critical point at a certain temperature $T^* > T_m$, which is destroyed by frustration [85]. When the liquid is cooled down, it starts to form locally preferred structures (LPS) in preparation for the transition at T^* , but those structures are incapable of tiling the whole space due to frustration, so they end up forming domains of size ξ separated by topological defects, where a surface tension will be located due to the mismatch. The rearrangement of these domains, not much differently from what happens in the mosaic picture, will then have to proceed by activation [85], producing a slowdown of the dynamics like the one observed in glass formers [86].

2.2.2.1 Models

The scenario suggested by FLD can be implemented in statistical-mechanical models. A particularly elegant realization in the case of spheres is the one proposed by Nelson [87]: the idea is to embed the spheres in a spherical manifold with $d = 3$, in such a way that the local icosahedral order is now compatible with extension in space. The energy of the system can then be minimized and a “reference” configuration obtained. The curvature of space is then reduced, up to the point when the euclidean flat space is recovered. This way one can observe how the ordered configuration on the sphere changes to a disordered configuration rife with FLDs, separated by a complex network of defects. However, this approach is also technically very hard to implement and it is almost impossible to get quantitative predictions [1].

There are two other possible ways: either a phenomenological scaling treatment, like the one implemented in [85], or coarse grained lattice models. The Hamiltonian of such models is always made up of two terms: one that reproduces the unfrustrated system and yields the second-order transition at T^* , and another which acts as a source of frustration. A paradigmatic Hamiltonian is

$$H = -J \sum_{\langle ij \rangle} S_i S_j + Q \sum_{i \neq j} \frac{S_i S_j}{|x_i - x_j|}, \quad (2.37)$$

where we can clearly see the competition between ferromagnetic, local interaction (which will tend to favor local ordering) and the long-ranged Coulombic interaction which acts as a frustrating term. Models of this sort can be defined with soft spins, Ising spins, $O(N)$ spins and Potts variables. In the case of $O(N \rightarrow \infty)$ and soft spins one can see that the transition is killed as soon as $Q \neq 0$ [88], while in the case of Ising spins the transition becomes first order [89]. Anyway, in both cases, a disordered phase is found at low T wherein dynamics is slowed down in a glassy manner [83]. The size ξ of FLDs in particular is found to have the scaling

$$\xi \simeq \sqrt{\frac{J}{Q}} \xi_0^{-1}, \quad (2.38)$$

where ξ_0 is the correlation length of the avoided transition at T^* . Since it decreases as the system is cooled below T^* , the size of FLDs is found to increase on lowering T , which in turn means that the barrier to rearrangement of the FLD must increase upon supercooling. So FLD theory passes the test as RFOT and DFT, since it does provide a good explanation for the super-Arrhenius increase of the relaxation time.

We can also observe from the (2.38) that more frustration means smaller FLDs. This is reasonable, since frustration keeps the FLDs from tiling the whole space, so having more of it should correspond to smaller domains. This in turn implies a direct relation between fragility and frustration, which is probably the most original prediction of FLD theory. As a result, FLD can account for a wide range of different behaviors, from strong to fragile, just by tuning suitably the strength of frustration.

2.2.2.2 Strengths and Weaknesses

FLD theory has the great merit of actually posing deep questions about the nature of cooperative regions seen in glassy systems. RFOT just postulates them as originated by an underlying disordered FEL, and DFT only focuses on how they move. FLD instead describes them explicitly, in a very practical and very grounded way, and proposes a coherent and elegant picture for their origin. FLD has also the merit of bringing back the attention of researchers on a fact so obvious it is often forgotten: glasses behave like solids, and the rigidity of solids is indeed due to structure, not dynamics, so perhaps it is too soon to rule out the existence of any structure in glassy materials: they may actually hide more order than we think (see for example [90]).

This grounded and real-space bound description of FLD theory is, however, also its weakness: as of now there have not been any direct observations of FLDs [1, 19]. We have focused before on how the static structure factor $S(\mathbf{q})$ does not seem to capture anything unusual on crossing T_g , although the fragmentation in FLDs could be so severe that the residual order eludes a bulk tool like the $S(\mathbf{q})$. In principle it could be possible to observe FLDs and their related LPSs through numerical simulations, but this is more complicated than it looks [91], and there is not even agreement on which is the locally preferred order one should look for. For example in [92], the growth

of icosahedral order is found to be more pronounced in fragile liquids as expected from the FLD approach, but in [93] it is argued that everything can be understood in terms of bond-orientational order, rather than icosahedral, so that the situation looks very convoluted.

Moreover, one would also appreciate to go beyond scaling arguments and coarse-grained models like the one defined in Eq. (2.37), and perform calculations on microscopic models of glass formers, but this does not look easy. It is indeed possible to implement numerically a Nelson-like treatment for a Lennard-Jones mixture [94] with very encouraging results, but at present there is no apparent way of translating this into a statistical-mechanical calculation. As a matter of fact, models like the one in Eq. (2.37), when treated with the replica method, show a Kauzmann transition like the one predicted in RFOT (see for example [95]), so it could very well be that a first-principles treatment of FLD will end up giving back RFOT results, which could be a very interesting turn of events.

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