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## Abstract

Supercooled liquids become increasingly sluggish upon cooling down to the glass temperature  $T_g$  where they can no longer be studied in equilibrium on the laboratory scale and behave as off-equilibrium amorphous solids, i.e., glasses. Simple activated dynamics account for the behavior of so-called strong liquids, but deviations from Arrhenius behavior are observed in fragile ones and have defied explanation for decades. Technical advances in experiments have steadily unveiled more facets of the puzzling phenomenology of fragile liquids including notably two-step relaxation, stretched exponentials, superposition principles, and dynamical heterogeneities. Theoretical efforts have developed mainly around the idea that some sort of finite-temperature critical phenomenon is at play, the key role in the discussion being played by two different critical points. The first one is thought to occur above  $T_g$ , and therefore it is not really a phase transition

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but rather a dynamical crossover. Numerical studies have shed much light on its nature, and nowadays it is largely believed to be the outcome of the smoothing of a sharp singularity spuriously predicted by mode-coupling theory. The existence of a dynamical crossover is largely accepted, and what is disputed is whether that is the end of the story.

Those who believe this is not the case typically put forward the classic hypothesis of a true thermodynamic phase transition to an amorphous glass state at some finite temperature below  $T_g$ . Originally suggested by elementary extrapolations of experimental data, this putative critical point is nowadays supposed to be a complex and fascinating object, notably the locus of a configurational entropy crisis accompanied by a divergent static correlation length. The quest to establish its existence, reinvigorated by the discovery of the glass/spin-glass analogy, is very much open but has produced nonetheless significant advances both at the theoretical and numerical level. Opponents of the thermodynamic transition scenario include notably those who advocate for dynamic facilitation, as realized in kinetically constrained models, to explain physics solely in terms of a dynamical crossover. Understanding dynamics between the crossover temperature and  $T_g$  would help assess both the range of validity of a description in terms of the crossover and whether something qualitatively different must be invoked close to  $T_g$  and below. Here the essential missing piece of information is the nature and spatial extent of the activated processes that should rule the dynamics: at the theoretical level, a consistent, beyond phenomenological, theory of these dynamical processes has still to be developed; at the experimental level, current techniques do not have enough spatial resolution; finally numerical simulations have been typically confined to higher temperatures due to hardware speed limitations but are beginning to access the crossover region and may provide some guidance in the coming years.

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## 1 Introduction

In spite of decades of experimental, theoretical, and numerical studies, the glass problem is very much open: the community agrees only on a few statements while all the rest is strongly debated. In the following an introductory critical discussion will be given of some of the theoretical and numerical results inspired by the idea that some sort of critical phenomena determines the puzzling phenomenology of supercooled liquids. The reader should be aware that this covers only a part, although significant, of the literature of this field. In the spirit of the handbook, this contribution is not intended as a general and exhaustive review but rather as an, hopefully stimulating, introduction to some of the main open questions. The interested reader will find in the references a number of more technically detailed review papers and books (Gotze 2009; Cavagna 2009; Wolynes and Lubchenko 2012; Berthier et al. 2011; Berthier and Biroli 2011).

This line of research has evolved over the years around the existence of two critical temperatures: the crossover temperature and the Kauzmann temperature. The first critical temperature occurs upon supercooling the liquid when it still can be studied in equilibrium, and its existence is largely agreed upon and can be considered part of the phenomenology. The problem is that it does not mark a genuine phase transition but rather a dynamical crossover; thus it is difficult to make sharp and universal statements about it. In this context mode-coupling theory (MCT) captures the initial steps of the dynamical slowing down but fails spectacularly because it predicts a sharp transition instead of a crossover, and the main open problem is to extend it to the crossover region and below. From the point of view of material modeling and simulations, it is a particularly important problem, because the resolution of current experiments cannot provide guidance for its solution. On the other hand, microscopic details are fully under control in numerical simulation, but hardware constraints limit them to considerably higher temperatures than those reached by experiments. Nevertheless many believe that the crossover region is attainable with present or near-future technology and hope to finally understand this regime in the coming years.

It is fair to say that our shared understanding of the physics of glasses ends with MCT slightly before the glass crossover. Below it we only know that some kind of activated dynamic should set in. In this context a fascinating but strongly debated hypothesis is the occurrence, at very low temperatures, of a genuine thermodynamic transition from the liquid to an amorphous glass state. This line of research has inspired a variety of novel analytical and numerical techniques; the idea is that the information on slow dynamics can be obtained without performing molecular dynamic simulations but rather by studying the equilibrium configurations of appropriately constrained systems. From the analytical point of view, the advantage is that one can perform static computations that are typically easier than full-fledged dynamical ones. From the numerical point of view, the advantage is that equilibrium configurations can be obtained through more efficient algorithms than molecular dynamics. This is a field where numerical work has been going on in the last 15 years, and significant recent developments include algorithms to reach temperatures that even experiments cannot. Nevertheless evidences for a genuine phase transition are still not decisive; besides this information has not shed light into the fundamental question of why dynamics becomes so slow.

This work is organized as follows. In order to define the problem, the main dynamical features of realistic supercooled liquids as obtained from experiments will be summarized in Sect. 2. In Sect. 3 the MCT scenario will be presented, and it will introduce a discussion of the extent to which the phenomenology can be explained in terms of an avoided MCT-like transition. Section 4 is devoted to the existence of a genuine phase transition occurring in the regime that is not accessible by experiments and to the conceptual, technical, and numerical developments it has inspired. Conclusions will be drawn in the last section.

## 2 Phenomenology of Supercooled Liquids

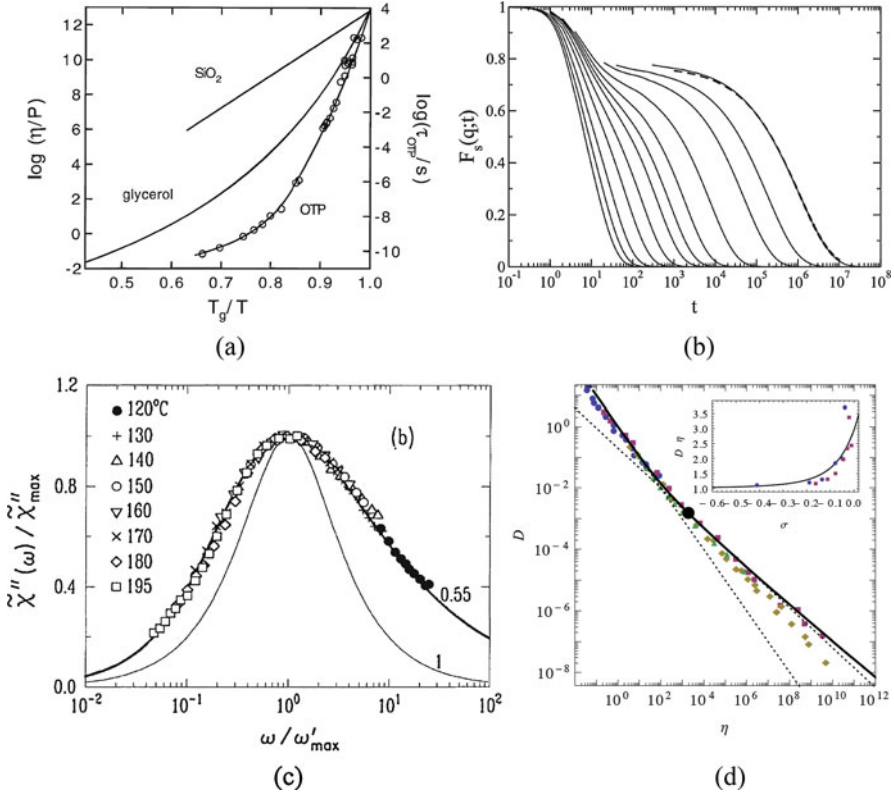
The main properties of supercooled liquids, as observed in experiments, are (1) power law to exponential crossover, (2) two-step relaxation, (3) complex dynamics (stretched exponentials), and (4) dynamical heterogeneities (violation of the Stokes-Einstein relationship (SER)). These are dynamical properties that a consistent theory of glasses should necessarily explain. In addition there are the so-called thermodynamics/dynamics correlations whose significance in relationship to the experimental dynamical features is more disputed.

The power law to exponential crossover is the oldest property that has been observed and possibly the most important. Upon slowly cooling a liquid crystallizes at the melting temperature. If one is able to further lower the temperature avoiding crystallization, a supercooled liquid is obtained. Upon further cooling, the relaxation time or equivalently the viscosity of the supercooled liquid increases up to a value where the viscosity is equal to a (conventional) value of the order of the laboratory timescale. This point defines the glass transition temperature  $T_g$ . It should be clear that nothing special happens at  $T_g$  from the point of view of the system; it is just the lowest temperature where the system can reach equilibrium in a timescale acceptable to humans. Obviously there is nothing strange in dynamic slowing down upon lowering the temperature; for instance, this occurs if dynamics proceeds through elementary events that require to overcome a constant free energy barrier  $E$ . In this case Arrhenius behavior is observed, with the logarithm of the relaxation time (or equivalently the inverse of the viscosity) increasing as the inverse of the temperature:

$$\tau_\alpha \propto e^{-\frac{E}{k_B T}} \quad (1)$$

Strong liquids exhibit by definition Arrhenius behavior upon supercooling, while fragile liquids exhibit a different behavior: when the logarithm of the viscosity is plotted vs. the inverse temperature in the so-called Angell's plot (1995), the data do not follow a straight line (see Fig. 1). In the early stages of supercooling, the viscosity of fragile liquids increases slowly and can be fitted by the tail of a power law diverging at some finite temperature. This temperature, however, marks a dynamical crossover: close to it the viscosity deviates from the power law and does not diverge; however it begins to increase in a more pronounced way that can only be fitted with functional forms depending exponentially on the temperature variations. Overall the data of fragile liquids exhibit a more or less pronounced bending with respect to the straight line Arrhenius behavior, and the slope at  $T_g$  provides a quantitative definition of kinetic fragility (note that this terminology has nothing to do with the brittleness properties of the corresponding glass). Experimental data above  $T_g$  have been fitted by many different functions, including some that, upon extrapolation, predict a divergence of the relaxation time at some finite temperature below  $T_g$ , notably the Vogel-Fulcher-Tammann (VFT) law:

$$\tau_\alpha = \tau_0 \exp \left[ \frac{DT_0}{T - T_0} \right] \quad (2)$$



**Fig. 1** Phenomenology of supercooled liquids. (a) Strong liquids like silica ( $SiO_2$ ) follow a straight line on the Angell’s plot, while fragile liquids like glycerol and *ortho*-terphenyl (OTP) exhibit a bending (Ediger et al. 1996). (b) The self-intermediate scattering function  $F_s(q; t)$  for  $q = 6.1$  at various temperatures from a numerical simulation of a binary mixture, from Flenner and Szamel (2013). The dashed line is a stretched exponential. (c) The susceptibility spectrum of supercooled CKN (Li et al. 1992) is broader than that of a single exponential (solid line); correspondingly the relaxation can be only fitted by a stretched exponential. (d) Diffusion coefficient  $D$  versus viscosity  $\eta$  for experimental and numerical simulation data from Rizzo and Voigtmann (2015). Dashed lines indicate  $D \propto \eta^{-1}$  (Stokes-Einstein relation) and a fit with  $D \propto \eta^{-0.65}$  (fractional SE relation). A large circle marks the crossover temperature. Inset:  $D \cdot \tau$  with simulation data

This leads to the two following essential questions: what causes the power law to exponential behavior in fragile liquids? Will the relaxation time eventually diverge at a finite temperature below  $T_g$ ?

Models of supercooled liquids are often defined in terms of spherical particles interacting with pairwise potentials, and the typical dynamical observable is the intermediate scattering function:

$$F(q, t) \equiv \frac{1}{N} \langle \rho_q(t) \rho_{-q}(0) \rangle \tag{3}$$

where the square brackets mean thermal average,  $\rho_q$  is the Fourier component of the density,

$$\rho_q \equiv \sum_{j=1}^N e^{i q r_j} \quad (4)$$

and  $r_j$  is the position of particle  $j$ . The intermediate scattering function is equivalent, by means of Fourier transforms, to the dynamic structure factors and the van Hove function. At  $t = 0$  the intermediate scattering function is equal to the static structure factor and relaxes to zero at large times. In experiments this quantity is accessible through a number of techniques (Richert 2012; Lunkenheimer et al. 2012). Observation of the two-step relaxation requires measurements on a huge range of timescales. The main relaxation, associated with the viscosity, is called the  $\alpha$  process hence the name  $\tau_\alpha$  for the relaxation time. However, there is an additional timescale  $\tau_\beta$  over which  $F(q, t)$  develops a plateau when plotted vs.  $\log(t)$  and the system appears to be essentially frozen. The  $\beta$  scale is orders of magnitude smaller than  $\tau_\alpha$ , but it is considerably larger than the microscopic timescale. In Fig. 1b the phenomenon is displayed as measured in a numerical simulation for the relaxation of the self-intermediate scattering function (the Fourier transform of the single-particle displacement). The origin of the two-step relaxation is often attributed to the emergence of caging (Gotze 2009). The idea is that when dynamics is sufficiently slow, the environment of a given particle appears to be frozen, and therefore the particle itself is caged and will in turn cage its neighbors.

Caging is observed clearly in numerical simulations of hard-sphere systems (Kob 1999), but its origin is not completely understood. In these systems the temperature can be always reabsorbed into a rescaling of times, and the only nontrivial external parameter to be changed is the density. It seems natural that upon increasing the density at some point dynamics will slow down because of reduced volume effects. The problem with this interpretation is that caging is observed already at rather low density, and it appears abruptly in a rather narrow range of densities, meaning that if one inspects instantaneous configurations it is rather difficult to tell the difference between a configuration from a system that displays caging and one from a system that does not. This is an aspect of the so-called structure vs. dynamics problem. In other words the question is whether slow dynamics can be traced back to some structural property of the instantaneous equilibrium configurations. We may ask if there is some observable that can be measured on a given configuration that will correlate with the fact that relaxation from that configuration will exhibit caging or not. This is a fundamental question in the field, and the negative answer amounts to say that glassiness is a completely dynamical problem; this issue will be discussed again later on.

In simple Arrhenius dynamics relaxation decays exponentially in time. Relaxation in fragile liquids instead is complex, meaning that can only be typically

fitted with a stretched exponential form  $\exp(-t^b)$ . In experiments this result in the broadening of the susceptibility spectra that are related to the Fourier transform of the relaxation (see Fig. 1c). Much as the two-step relaxation, this is not at all trivial. As soon as the relaxation is controlled by independent microscopic events occurring in a uniform environment, the decay is necessarily exponential, while in order to have a stretched exponential behavior, one must either invoke spatial fluctuations in the environment or a moderately large correlation length implying that the relaxation events are not elementary or involve many particles. Which hypothesis is correct, if any of the two, is at present unknown. *Superposition principles* are an additional nontrivial feature of the relaxation. Strictly speaking they amount to say that the temperature dependence of the relaxation is only encoded in the timescale  $\tau_\alpha$ , meaning that one can write

$$F(q, t) = C_q(t/\tau_\alpha) \quad (5)$$

for some function  $C_q(t)$ . This property is verified approximately by many supercooled liquids in some temperature range; see Gotze (2009) for a more detailed discussion of experimental data.

In the last 20 years dynamical heterogeneities (Ediger 2000; Berthier et al. 2011) have emerged as a fundamental property of fragile liquids. In short the idea is that approaching  $T_g$  if one look at the liquid at the microscopic level there will be regions where dynamics is orders of magnitude faster than in the rest of the system. The above generic statement can, and often is, misinterpreted if one does not give it a more quantitative formulation. This is given by the so-called violation of the Stokes-Einstein relationship (SER) connecting the viscosity with the inverse of the diffusion constant of a given particle. The SER is verified at high temperatures, but violations are observed approaching  $T_g$  and starting somewhere near the crossover temperature (see Fig. 1d). The SER can be justified assuming that each particle perform a kind of Brownian motion in a homogeneous environment. Conversely violations should occur in a situation in which, even if the SER is satisfied locally, the environment is not homogeneous and the local viscosity has strong fluctuations in such a way that the inverse of its average is different from the average of its inverse. Once again the precise mechanism leading to SER violations is not agreed on, but they are definitively considered a hallmark of complex dynamics. MCT helps to clarify that dynamical heterogeneities should not be confused with dynamical fluctuations; indeed MCT has diverging dynamical fluctuations but no SER violation.

In addition to the above dynamical features, a consistent part of the literature points toward the so-called thermodynamics/dynamics correlations connecting dynamical quantities like the viscosity with thermodynamical quantities (the entropy) measured by calorimetry. They are often invoked in the context of theories that advocate for the existence of a genuine phase transition below  $T_g$ , and they will be discussed in more details in Sect. 4.

### 3 The Crossover Temperature

#### 3.1 Mode-Coupling Theory

Mode-coupling theory (Gotze 2009) starts from the exact microscopic equations for the dynamic structure factor of simple monoatomic liquid models and then makes a certain number of approximations. The outcome is a set of closed equations that can be solved numerically once the static structure factor is provided as input. Before discussing MCT predictions, let us stress that there is at present a very poor understanding of the approximations involved. The only justification comes a posteriori as the results display a significant agreement with the behavior of actual systems (again with some caveats), and the problem is complicated by the fact that some of the approximations involved cannot even be tested directly. Therefore, in spite of the fact that MCT starts from the exact microscopic dynamics, it is fair to say that it is essentially a black box whose internal operation is unknown. Efforts to understand it have been limited in the past, and more work should be devoted to this essential open problem. Instead research activity has essentially ignored this issue focusing on the empirical development of a sort of operating manual of the theory and applying the resulting procedure to a variety of models and systems again with impressing results.

There is a broad agreement that many supercooled fragile liquids can be modeled by simple liquids with pairwise interactions, including hard-sphere (HS) systems. However in two and three dimensions, monoatomic systems tend to crystallize easily and cannot be supercooled to very low temperature; therefore one must consider, at least, binary mixtures (Kob 1999). Mode-coupling equations can be extended to binary systems of hard or soft spheres, and the resulting equations can be solved to obtain the dynamic structure factor giving as input the static structure factor typically obtained from numerical simulation.

The theory predicts that at a given value of the control parameter (temperature or pressure), dynamical arrest occurs meaning that the infinite time limit of the dynamic structure factor does not decay to zero as it should in the liquid phase but tends to a constant momentum-dependent value, called the non-ergodicity parameter. As we said already it is known that this prediction is completely wrong, and in order to understand why, in spite of this dramatic failure, MCT is still considered highly valuable; we have to discuss its predictions upon approaching the transition temperature  $T_{MCT}$ .

First of all, MCT predicts that the decay of the dynamic structure factor proceeds in a two-step fashion as seen in experiments, with both scales  $\tau_\beta$  and  $\tau_\alpha$  diverging as power law of  $\tau \equiv T_{MCT} - T$ . More precisely at the critical temperature  $T = T_{MCT}$ ,  $F(q, t)$  approaches the nonzero long-time limit  $F_c(q)$  in a power-law fashion with a nontrivial exponent  $a$ :  $F(q, t) \approx F_c(q) + c/t^a$ . The exponent  $a$  controls the divergence of the  $\beta$  scale through

$$\tau_\beta \propto |\tau|^{-\frac{1}{2a}}. \quad (6)$$



For temperatures slightly larger than  $T_{MCT}$ ,  $F(q, t)$  reaches the plateau value  $F_c(q)$  in a finite time that defines the scale  $\tau_\beta$ . For times of the order of  $\tau_\beta$ , it remains close to the plateau value up to deviations of order square root of  $\tau \equiv T_{MCT} - T$  before eventually leaving the plateau on the scale  $\tau_\alpha \propto |\tau|^{-\gamma}$ . The decay on the  $\alpha$  scale satisfies both the superposition principle and the stretched exponential form with exponent  $\exp[-t^b]$ , in striking agreement with experiments. Furthermore the exponent  $\gamma$  is related to  $a$  and  $b$  through

$$\gamma = \frac{1}{2a} + \frac{1}{2b} \quad (7)$$

and the two exponents  $a$  and  $b$  can be both expressed as

$$\lambda = \frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)} \quad (8)$$

where  $\lambda$  is the so-called parameter exponent for which MCT provides quantitative predictions.

Data from numerical simulations of a variety of models are consistent with this scenario in some range of temperatures (Kob 1999; Gotze 2009). In particular, it is often possible to estimate the critical temperature, the exponents, and the ergodicity-breaking parameter  $F_c(q)$  and compare them with the quantitative predictions of MCT. One should bear in mind that these estimates from realistic systems data are intrinsically arbitrary because in principle MCT scalings are only well defined close to the dynamical arrest transition, but in practice the transition does not occur. In practice this ambiguity is reflected by the fact that the critical temperature depends on the observable and also on the nature and range of the fit. In spite of this intrinsic ambiguity, it turns out that the range of variations of the critical temperature is often sufficiently small for the whole procedure to make sense. This happens for most models and experimental systems, and indeed this *experimental* MCT critical temperature (or density) is almost always reported in any study of supercooled liquid. Furthermore the value of the ergodicity-breaking parameter can be obtained from the data, and it is often in excellent quantitative agreement with the predictions of MCT. The values of the critical exponents are more ambiguous but still are in good agreement with the predictions of MCT. In particular it seems that there is good consistency between the exponents  $a$  and  $b$  that control the  $\beta$  regime with the exponent  $\gamma$  that controls the  $\alpha$  regime. This is a manifestation of the nontriviality of the double-step relaxation, in the sense that processes occurring on large but comparatively very different timescales are related. It is worth mentioning that MCT predictions appear to be somewhat meaningful even below the critical temperature  $T_{MCT}$  where the theory predicts that  $F(q, t)$  have a nonzero long-time limit increasing as  $\sqrt{\tau}$  for  $T$  smaller than  $T_{MCT}$ . It turns out that in many experimental systems and numerical simulations a square root increase of the plateau value can be actually observed notwithstanding the fact that  $F(q, t)$  will eventually leave the plateau at variance with MCT predictions.

Overall the comparison between numerical simulations and theory suggests a scenario in which ideal MCT predictions are accurate except very close to the critical temperature where the theory needs some substantial modification. Unfortunately this scenario is too optimistic in the sense that the effective MCT temperature, the one for which MCT fits do describe actual data, is definitively different from the value of the critical temperature obtained from the solutions of the MCT equations itself (Kob 1999). This discrepancy is model-dependent but seems rather universal; typically it is more pronounced in soft sphere models than in HS, but its origin is unclear. As a result, it is often said that the MCT critical temperature is wrong, but it should be clear that there are two essentially different aspects of it being wrong. In a weak sense it is wrong because its value does not compare well with the value used to fit numerical data. The theory overestimates this value, and in practice in order to obtain reasonable fits, one must plug into the MCT equations the structure factors from higher temperatures. In a strong, more fundamental, sense MCT is wrong because there is no true critical temperature in experiments and numerical simulations.

The above discussion on the critical temperature allows to introduce the quantitative vs. qualitative MCT scenario. There are some features of MCT that are more universal and are found also outside the original domain of the theory, i.e., supercooled simple liquid models in physical dimension. The most striking instance is the case of spin glasses displaying one step of replica symmetry breaking (1RSB) in Parisi's scheme (Mezard et. al. 1988). These systems are utterly different from a liquid at the microscopic level; notably they are defined on a lattice, and they have quenched disordered interactions, and yet, as discovered by Kirkpatrick and Thirumalai (1987), their dynamics shares the very same phenomenology of MCT, namely, dynamic arrest characterized by two-step relaxation with power-law divergent timescales. Furthermore in the  $\beta$  regime, where the correlation stays near the plateau, dynamics obeys the very same critical equation of MCT, i.e., a universal quadratic dynamical equation that does not depend on the microscopic details of the model. Thus one should always bear in mind that there are qualitative, much more general, MCT predictions and quantitative MCT predictions that are only limited to supercooled liquid models. In MCT literature this distinction is often not very clear.

An important instance of the qualitative/quantitative difference is the case of simple supercooled liquids in large dimension. This problem has been investigated extensively over the years under the expectation that in infinite dimension the crossover should become a true transition and the problem should become solvable. These studies culminated recently with the exact and complete solution (Charbonneau et al. 2016) that confirmed that the qualitative MCT scenario is correct (e.g., the relationship between the exponents holds), while the quantitative values of the critical temperature and of the exponents are wrong.

Another striking instance of the universality of the qualitative MCT scenario is provided by cooperative kinetically constrained models (KCM) (Ritort and Sollich 2003; Chandler and Garrahan 2010) that will be briefly discussed in the next

section. Remarkably the Fredrickson-Andersen model, when studied on the (mean-field) Bethe lattice, displays a dynamical arrest transition in agreement with the qualitative MCT scenario (Berthier and Biroli 2011). Note that this statement is only based on numerical observations, and justifying it analytically is a fascinating open problem.

We are now in position to discuss the failures and successes of MCT in connection with the phenomenology of real supercooled liquids presented in the previous section. The two-step relaxation scenario is a significant success together with the presence of stretched exponentials in the relaxation. The main failure is the prediction of a true phase transition which in reality is a crossover; however MCT is at least consistent with the initial power-law behavior. Another significant failure of MCT is that even close to the critical temperature, it does not display the SER violations associated with dynamical heterogeneities. By means of the microscopic MCT equations, one can indeed obtain predictions for the diffusivity. Remarkably the lack of SER violation is confirmed by the exact solution in infinite dimension (Charbonneau et al. 2016). The fact that SER holds in MCT does not mean that dynamical fluctuations are finite within the theory. Actually one can argue that close to  $T_{MCT}$  the theory predicts both diverging dynamical fluctuations and diverging dynamical correlation length. This can be shown by means of an extension called inhomogeneous MCT (Berthier and Biroli 2011) although care must be taken in extracting the critical exponents as simple scaling arguments lead to incorrect results (Rizzo 2014). Given that the dynamical arrest transition does not occur, these divergences are also unrealistic and are not often emphasized in the MCT literature.

A few comments on the spurious divergence of the dynamical correlation length are in order. In the early days of MCT, it was not clear what was the origin of dynamical arrest, and some authors believed that no diverging correlation length was involved (see, e.g., Ediger et al. 1996). One can argue on physical ground that for ergodic statistical mechanics systems, a finite-temperature dynamical transition must be necessarily associated with a diverging correlation length (these arguments can be made rigorous in the case of spin-glass models (Berthier and Biroli 2011)). This observation may appear not so important in the case of the MCT crossover because in the end no dynamical arrest transition is present, but it is important when discussing the possibility of a true transition occurring at some finite temperature below  $T_g$  as we will see in the following section. Another point worth mentioning is that while diverging fluctuations must be necessarily accompanied by a diverging correlation length, a simple increase of fluctuations does not imply an increasing correlation length. This is important to assess the relevance of experimental measurements of nonlinear susceptibilities. The increase of fluctuations reported in these experiments is sometimes interpreted as an indication of an increase of the correlation length (Albert et al. 2016), overlooking the fact that the connection between the two quantities requires additional assumptions. Actually a recent theory of the crossover provides a counterexample in which increasing dynamical fluctuations are accompanied by a decreasing correlation length (Rizzo 2014).

### 3.2 Toward a Theory of the Crossover

The understanding of supercooled liquids ends slightly above the crossover temperature and everything occurring below is disputed. While MCT is definitively wrong at low temperatures, its success at moderate supercooling suggests that one should amend it in order to describe the crossover region and then move to even lower temperatures. Efforts in this direction have been going on for a long time, but none is considered fully satisfactory and will not be discussed in detail. People tried often to modify the theory at the microscopic level. In general it turns out to be rather easy to remove the sharp transition, but this typically leads to a simple exponential relaxation thus spoiling the stretched exponential which is one of the great successes of MCT, not to mention that these modifications are always ad hoc and phenomenological. Note that MCT also starts from the microscopic first-principle description and then makes some uncontrolled approximations, however there is no evident logical connection between the approximations made and the final results, and in this sense MCT approximations are not considered ad hoc.

A different possibility is that in order to describe the physics at the crossover and go beyond MCT, one should use instead a mesoscopic effective theory that is accurate on a coarse-grained scale over which the microscopic details of the model are unimportant. This is the way to proceed in the case of a genuine second-order phase transition because they are characterized by a divergent correlation length. Applications of these ideas in the context of the crossover appear counterintuitive, since in the end the correct theory should tell us that there is no divergence of the correlation length. Nevertheless one should note that in order for a mesoscopic effective theory description to be valid, one does not need a diverging correlation length; it is enough for it to be large compared to the microscopic scale. On the other hand it is largely agreed that dynamics in the crossover region is cooperative meaning that the dynamical correlation length, while not diverging, is indeed large (Berthier and Biroli 2011; Harrowell 2011).

The mesoscopic theory can be shown to be equivalent to a solvable model of dynamical stochastic equations. Quite interesting the resulting model displays all the hallmark of supercooled liquid, namely, the power law to exponential crossover, two-step relaxation, stretched exponential, and dynamical heterogeneities in the form of SER violations (Rizzo 2014). Most importantly it is not a phenomenological theory because these features are not the outcome of ad hoc assumptions. On the other hand, by definition, there is no way to tell from the mesoscopic theory itself if it is appropriate to describe a specific system. For that one should start from a first-principle microscopic description and apply coarse-graining in a rigorous way. This implies that in principle this description could be accurate for one system but not for another system. It is also important to note that the validity of a mesoscopic description for a given supercooled liquid model could also be assessed explicitly by means of a numerical simulation. This requires to accurately measure dynamical fluctuations and correlation lengths to check if the order parameter after coarse-graining is sufficiently smooth to be described by an effective theory.

The technology to measure dynamical correlations and fluctuations was developed some 20 years ago motivated by the experimental observations of dynamical heterogeneities (Berthier and Biroli 2011), and it is known that extracting these quantities from numerical simulations is quite demanding.

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## 4 Dynamics vs. Thermodynamics: The Kauzmann Temperature

The idea of a genuine phase transition occurring below originated with Kauzmann's analysis of calorimetric experimental data (Kauzmann 1948). He noticed that while at the melting temperature the entropy of the crystal is lower than that of the liquid, it decreases less upon cooling in such a way that, by extrapolation, they should become equal at a temperature  $T_K < T_g$ . In order to avoid the paradox of an amorphous state having lower entropy of the crystal, he considered various possibilities including that the liquid had a genuine phase transition to a thermodynamically stable glass state at  $T_K$ . Nowadays Kauzmann's observation is not considered a paradox anymore: in the late 1950s computer simulations showed, to the surprise of many, that an isolated liquid of hard spheres does crystallize, and this occurs precisely because the crystal state has a higher entropy than the disordered state! This is understood in terms of a balance between short-range and long-range entropies: the crystal has a smaller long-range contribution to the entropy but has a larger local contribution because the particles have locally more room than in the amorphous state (Ackerson 1993). As we said already, crystallization is actually a major problem in numerical simulations of supercooled liquids, and it is typically avoided using binary mixtures or more polydisperse systems.

In spite of the fact that Kauzmann's observation is not really a paradox, the debate over the existence of a genuine phase transition is still going on to this day. Interestingly Kauzmann himself was against this hypothesis and believed that the paradox would be solved by some dynamical mechanism. The main problem being that it is not possible to study the supercooled liquid below  $T_g$ . Another important aspect of the discussion is the observation of thermodynamics/dynamics correlations (Adam and Gibbs 1965). Adam and Gibbs pointed out that for many experimental systems VFT fits of viscosity data yield a critical temperature  $T_0$  compatible with the  $T_K$  extrapolated from calorimetric data. In particular if one plots the logarithm of the viscosity (a dynamical quantity) as a function of the inverse of the excess entropy, i.e., the difference between the entropy of the supercooled liquid and that of the crystal (a thermodynamic quantity), they appear to be correlated.

To complete the picture, Goldstein (1969) started with the observation that approaching  $T_g$  relaxation from a given initial configuration proceeds in a two-step fashion; first each particle explores its cage and then escapes from it. Then he argued that the motion inside a cage defines a sort of metastable state and the final relaxation can be seen as a jump from one metastable to another. If one further argues that the entropy of the metastable state corresponds to a kind of vibrational

contribution (essentially analogous to the crystal entropy), it follows that the excess entropy is a measure of the number of metastable states, called the configurational entropy. The decrease of the configurational entropy thus explains the slowing down of dynamics because the system in order to relax has less and less metastable states to escape to.

It is important to realize that while the excess entropy is a well-defined object that can be measured experimentally, the configurational entropy is not. Entropy is a static equilibrium concept and thus cannot be applied to a metastable state that can only be observed on a finite time window. More practically this is reflected by the fact that there is no unique definition of it. On the other hand, Kirkpatrick, Thirumalai, and Wolynes (KTW) pointed out that the previously mentioned mean-field spin-glass models are indeed characterized by the presence of many metastable states below a temperature  $T_{MCT}$  and the corresponding configurational entropy vanishes at some lower temperature  $T_K$  (Kirkpatrick and Thirumalai 1987). At the mean-field level there is simply no dynamics beyond  $T_{MCT}$ , and they put forward the idea that in physical dimension the mean-field picture should be modified invoking nucleation arguments as in the classic Becker-Doring theory.

Classical nucleation theory describes the decay of a metastable phase to the stable phase of lower free energy in terms of the expansion of droplets of the stable phase. The surface tension tends to shrink the droplet, while the bulk free energy difference tends to expand it. The two forces depend on the radius of the droplet and balance at some critical radius  $r_c$ : droplets larger than  $r_c$  will expand, while smaller droplets will shrink and disappear. The time to nucleate a critical droplet naturally increases with the size of the critical radius which in turn increases and diverges at the coexistence point where the free energy difference is zero and both phases are stable; correspondingly the lifetime of the metastable state diverges exponentially. The idea of KTW is to use nucleation arguments to describe the dynamics of supercooled liquids using the configurational entropy in place of the free energy difference. This offers an explanation of the thermodynamics/dynamics correlations and of the exponential VFT-like divergence of the relaxation time. Furthermore the nucleation argument implies that there is a diverging correlation length, which was already advocated by Adam and Gibbs that suggested that dynamics is driven cooperatively rearranging regions (CRR) of increasing size upon approaching  $T_g$ .

The existence of an actual phase transition at  $T_K$  is an appealing topic because it is a sharp statement, either true or false. On the other hand the nontrivial phenomenology we need to explain is observed *above*  $T_g$ , and thus a consistent part of the community does not consider it particularly relevant. At any rate, even if a genuine glass transition occurred below  $T_g$ , one should still have to prove that the physics observed above  $T_g$  is a consequence of its presence. Instead many believe that the physics of supercooled liquid can be explained solely in terms of a crossover temperature that was discussed in the previous section. Note that in the context of mean-field theories, the existence of a  $T_K$  requires logically the presence of a crossover at a higher temperature while the opposite is not true: models exist for which there is an MCT singularity, but the configurational entropy does not vanish at any finite temperature.

The opposite view that dynamics may be completely unrelated to thermodynamics is supported by the so-called Kinetically constrained models (Ritort and Sollich 2003; Chandler and Garrahan 2010). They are defined in terms of binary variables (that can be viewed as spins) on a lattice. The variables do not interact and thus the thermodynamics is trivial at all temperatures. Dynamics instead must obey some constraint, for instance, in the well-known Fredrickson-Andersen model, each spin must have at least  $k$  neighbors in the up state in order to flip. It turns out that dynamically these models display many of the phenomenological features of supercooled liquids, notably a power law to exponential crossover and two-step relaxation. Since no thermodynamics transition may occur in these models, their physics is typically interpreted solely in terms of the existence of a crossover temperature. Furthermore on the Bethe lattice they seem to display a sharp MCT-like transition, and the aforementioned dynamical features can clearly be associated with this transition being avoided on lattices in three and two dimensions (Berthier et al. 2011). The main open problem is that these models lack a clear microscopic connection with the original liquid models, and it is not exactly clear how the constraints on the dynamics should emerge from the (unconstrained) microscopic Hamiltonian dynamics. In practice this is also reflected by the impossibility of obtaining some sort of quantitative prediction. Another problem is that it seems difficult to rationalize the Adam-Gibbs phenomenological correlations between dynamics and excess entropy using these models, although, as we said before, one may question their overall relevance.

An additional interesting open problem is inherently associated with facilitation dynamics. At low temperatures one expects that in a supercooled liquid there are large regions that are essentially frozen for a large amount of times and eventually relax. One possible mechanism inducing the relaxation is the expansion/motion of a mobile region from outside the blocked region into it, but one can also think of relaxation led by thermally activated rare events. However this second mechanism is impossible in KCM where relaxation can only propagate from the borders of the blocked region. Thus knowing what is the mechanism at work in actual supercooled liquids could help discriminate between competing theories, but at present this is unclear.

From a practical point of view, the idea of a genuine thermodynamics transition is appealing because one can study it in a purely static framework. In the context of numerical simulations, one is no longer bound to use a physical algorithm to thermalize the system, and more efficient algorithms can be devised. For instance, particle-swap algorithms have been used in the last 15 years and recently have produced spectacular results for specially designed polydisperse hard-sphere mixtures that were thermalized up to densities corresponding to the laboratory timescale and even below (Berthier et al. 2017).

Underlying any static study in the context of supercooled liquids is the key question of whether nontrivial information can be extracted solely from the instantaneous equilibrium configurations. At first one would say that the answer is no, after all one of the striking features of supercooled liquid models of hard or soft spheres is precisely the fact that if one looks at the instantaneous configurations



at various temperatures (or densities) approaching the crossover, one cannot detect any significant change that could justify the dramatic increase of the relaxation time. Nevertheless, guided by the supercooled liquid/spin-glass analogy advocated by KTW, various authors have suggested that nontrivial information can be obtained solely from the equilibrium configurations by applying appropriate procedures (Wolynes and Lubchenko 2012).

The general idea is that one has to use an equilibrium configuration of the original system (the reference configuration) to define a new system and then show that nontrivial information can indeed be read off the equilibrium configurations of the new system. The first procedure that was introduced is the so-called Franz-Parisi potential that counts the equilibrium configurations that are at some fixed distance from the reference configuration. At the mean-field level, the potential has a minimum as a function of the distance at the maximal distance but, upon lowering the temperature, develops a secondary minimum at  $T_{MCT}$ . The difference in height between the primary and the secondary minimum is the configurational entropy that will eventually vanish at a lower temperature. This mean-field picture must be modified in finite dimension by applying a Maxwell construction as in ordinary first-order phase transition: one expects that the potential first develops a constant-slope segment close to the crossover temperature with the slope eventually going to zero at  $T_K$ .

Another interesting procedure is to measure the so-called point-to-set length (Berthier and Biroli 2011). In this case the particle positions are frozen in the reference configuration except inside a spherical cavity that it is then thermalized again. One expects that when the cavity is very large the bulk should be insensitive to the constraint at the boundaries, while if the cavity is sufficiently small, the center of the cavity should be stuck in a metastable state (stabilized by the frozen boundary). The point-to-set length is defined as the length that separates these two regimes, and mean-field theory predicts that it should diverge at  $T_K$ . This length should provide a way to actually measure the size of CCRs thus rephrasing the KTW idea of a diverging correlation length in a way that is amenable to be tested in simulations.

Finally we can mention random pinning that amounts to freeze a finite fraction of the particles of the reference configuration and equilibrate again the remaining free particles (Berthier and Biroli 2011). In this case the existence of genuine phase transition can be linked to the presence of a line of first-order transitions in the temperature-concentration plane. Different geometries, e.g., the freezing/pinning of an infinite wall of the system, have also been studied. Note that in both the pinning and cavity procedure, it can be shown that the configuration in which the free particles have the same positions they had in the reference configuration is an equilibrium configuration for the constrained system, which is a considerable advantage because one does not need to equilibrate the system again.

In the last 20 years the above procedures have been applied to various systems, and the most spectacular results are those obtained recently by the swap algorithms (Berthier et al. 2017). In these studies both the Franz-Parisi potential and the



point-to-set length were measured in equilibrium for values of the density even higher than the glass density  $\rho_g$ . Their behavior was found to be compatible (through extrapolation) with the presence of an actual phase transition at some  $\rho_K$ . Unfortunately, as it will be discussed in the following, while being a tremendous improvement with respect to earlier studies, it seems that these results are not enough to assess convincingly the validity of the scenario.

One problem is that the degree of extrapolation that one has to make on the actual data is still significant, and if one thing can be learned from the extensive literature on glasses is that extrapolations are always debated. Another problem concerns the point-to-set length itself and emerged from the early numerical studies of this quantity. Measurements of this quantity indicate a rather small value that increases slowly; thus, while a divergence at lower temperature cannot be ruled out, it is not particularly remarkable. Given that the growth and eventual divergence of this quantity should be the driving mechanism behind the growth of the relaxation time, we have a problem because this length is small while the relaxation time is increasing exponentially. Therefore it is further postulated that the relationship between the static length and the relaxation time is exponential due to some kind of activation mechanism. To this day however, a solid theoretical foundation of these statements is lacking.

The connection with dynamic raises an additional problem. As we discussed in the previous section, the dynamical correlation length should diverge at  $T_{MCT}$ . In the region where it can be measured, it exhibits a significant growth, while obviously being nondivergent. However in the region where both can be measured, the dynamical correlation length is definitively larger than the point-to-set length and appears to be growing more strongly, such that extrapolation suggests that their difference would be even more pronounced at lower temperatures. In other words the static length does not seem to be relevant for dynamics in the region where dynamics is already nontrivial.

In order to complete the discussion on the relevance of static methods, one must add that unphysical algorithms may allow to assess the validity of supercooled liquid models. As we said already the problem of crystallization becomes less severe increasing the dimension, but in three and two dimensions one is necessarily forced to consider at least binary mixtures. Recent numerical studies suggest that even if they do not crystallize at the temperatures reached by state-of-the-art molecular dynamics simulations they will be at lower temperatures accessible at present only by unphysical algorithms. Furthermore while up to now the knowledge of low-temperature equilibrium configurations has not shed light into the central problem of why dynamics slows down, they could be used to study the emergence of various anomalies in the glassy state observed in experiments. Besides understanding why swap algorithms are successful may shed light into why physical dynamics is instead so slow.

Some comments are important on the analogy between spin glasses and supercooled liquids suggested almost 30 years ago by KTW. On general ground systems with a completely different microscopic structure can be expected to share some

common behavior if they have a sufficiently large correlation length, such that the relevant physics occurs on a scale insensitive to microscopic details. In this light the fact that static length measured is typically small is troublesome. Furthermore many problems concerning these spin-glass models are still open irrespective of their eventual connection with supercooled liquids. First of all there is no numerical evidence that any of these spin models actually displays an entropy crisis transition with a discontinuous order parameter in finite dimension: the fate of the MF transition in finite dimensional system has still to be firmly established. Various failures to identify such a model have been rationalized by noticing that short-length fluctuations, already present on finite-connectivity mean-field lattices, are responsible for the absence of the transition rather than long-length fluctuations that would be a more general and harmful mechanism. Thus the quest for a good candidate is still a fascinating open problem.

Besides the numerics, an additional problem is that there is no precise and well-established analytical treatment of finite dimensional effects. In particular the connection between statics and activated dynamics is not well established even at the mean-field level, i.e., that of nucleation theory for metastability and phase coexistence. Furthermore, in order to agree with experimental data, the phenomenological expressions require the use of non-mean-field exponents that nobody knows at present how to compute. Note that these are all well-defined problems that should be addressed and solved irrespective of their relevance to supercooled liquids.

We have seen that the static approaches offer a considerable advantage at the algorithmic level, but there are also major advantages at the analytic level, because dynamics is typically more difficult than statics. The spin-glass/structural glass analogy suggests that one has to use the replica method (Mezard and Parisi 2012) that indeed provides a way to compute static objects like the Franz-Parisi potential and the point-to-set length. In finite dimension the replica method predicts a MCT-like transition that should be considered a spurious mean-field modification of what is in reality a crossover. This follows from the fact that, as in MCT, one must resort to some approximation scheme. As we said before, MCT provides nevertheless good quantitative estimates for quantities like the ergodicity-breaking parameter and the (pseudo)critical exponents. On the contrary current approximation schemes in the replica method studies yield predictions of considerable lower quality. On the other hand, as we said in the previous section, the replica method has been used successfully to study supercooled liquids in infinite dimension. This is an instance, albeit special, of a system where the connection between dynamics and thermodynamics can be demonstrated starting from first-principle microscopic methods, to be contrasted with KCM models, where, at present, there is no explicit microscopic derivation of the assumption that dynamics is facilitated. Still, the essential problem remains to describe how the ideal MCT transition becomes a crossover in finite dimension, and it is not even clear if the mechanism at work in large but finite dimension is the same in dimension two and three.

## 5 Conclusions

The body of work presented in the previous sections may be summarized as follows: there is an accepted transition which is not really a genuine critical point, and then there is another transition that is really critical but whose existence is highly debated.

State-of-the-art molecular dynamics simulations can equilibrate a few super-cooled liquid models down to temperatures close and slightly below the crossover temperature. While there is no precise way to substantiate these claims as we are dealing with a crossover and not a sharp critical point, there is, nevertheless, a widespread belief in the community that the next generation of numerical studies will be able to probe the crossover region and beyond for a variety of models. This makes all the more urgent to go beyond MCT and develop a comprehensive theory of the crossover with qualitative and quantitative predictive power.

Additional motivation to tackle this problem comes from other critical phenomena that have not been discussed here. In particular in the context of MCT, higher-order glass-glass transitions have been predicted and also detected numerically to some extent (Gotze 2009). Actually, the ability to predict these singularities prior to observation has convinced many of the value of MCT and of the fact that one should try to correct its shortcomings instead of throwing it away altogether. Much as the MCT transition, these higher-order singularities are expected to become smooth crossovers in realistic systems, and it seems reasonable that their understanding would benefit from any development in the former. Similarly, the study of liquids in high dimension (Charbonneau et al. 2016) has suggested the existence of even more exotic critical points, notably full replica-symmetry-breaking critical points as observed in mean-field spin glasses. At present the relevance of these transitions in realistic models is unclear. Be as it may, they are intrinsically mean field in nature, and their existence in realistic models poses a number of conceptual problems. Actually they may be observed only after the MCT crossover has occurred, and it is likely their fate in finite dimension could be fully understood only once the crossover problem has been solved.

As for the debate on the existence of a genuine glass transition below  $T_g$ , the bottom line is that the static objects that should manifest critical behavior, e.g., static length scales, are compatible with a singularity, but their divergence is too mild and not particularly remarkable in the range where they can be measured in current numerical simulations. On the other hand their connection with the truly remarkable dynamical features is still speculative and should be established more rigorously. Nevertheless this is a field in which progress has been made steadily in the last decades and more is expected to come.

If we had to single out one fundamental open question from the previous discussion, that would be the nature of the activated process below the crossover temperature and above  $T_g$ . Measurements of increasing dynamical correlation lengths unambiguously show that kinetic fragility, i.e., the power-law-to-exponential crossover is induced by the dynamics becoming cooperative. The problem is what happens at lower temperatures: do correlation lengths continue to increase? Can dynamics

be described solely in terms of the crossover, or can we identify some feature that necessarily requires some other mechanism approaching  $T_g$ ? Currently, experiments do not have enough spatial resolution to shed light on these questions while the timescales involved are too large for numerical simulations, but both problems could be overcome in the future through some breakthrough.

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## References

- Ackerson BJ (1993) When order is disordered. *Nature* 365:11–12
- Adam G, Gibbs JH (1965) On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *J Chem Phys* 43(1):139–146
- Albert S, Bauer T, Michl M, Biroli G, Bouchaud J-P, Loidl A, Lunkenheimer P, Tourbot R, Wiertel-Gasquet C, Ladieu F (2016) Fifth-order susceptibility unveils growth of thermodynamic amorphous order in glass-formers. *Science* 352:1308
- Angell CA (1995) Formation of glasses from liquids and biopolymers. *Science* 267:1924
- Berthier L, Biroli G (2011) Theoretical perspective on the glass transition and amorphous materials. *Rev Mod Phys* 83:587
- Berthier L, Biroli G, Bouchaud J-P, Cipelletti L, van Saarloos W (eds) (2011) Dynamical heterogeneities in glasses, colloids, and granular media. Oxford University Press, Oxford
- Berthier L, Charbonneau P, Coslovich D, Ninarello A, Ozawa M, Yaida S (2017) Configurational entropy measurements in extremely supercooled liquids that break the glass ceiling. *PNAS* 114:11356–11361
- Cavagna A (2009) Supercooled liquids for pedestrians. *Phys Rep* 476(4–6):51–124
- Chandler D, Garrahan JP (2010) Dynamics on the way to forming glass: bubbles in space-time. *Annu Rev Phys Chem* 61:191
- Charbonneau P, Kurchan J, Parisi G, Urbani P, Zamponi F (2016) Glass and Jamming transitions: from exact results to finite-dimensional descriptions. *Annu Rev Condens Matter Phys* 8: 265–288
- Ediger MD (2000) Spatially heterogeneous dynamics in supercooled liquids. *Annu Rev Phys Chem* 51:99
- Ediger MD, Angell CA, Nagel SR (1996) Supercooled liquids and glasses. *J Phys Chem* 100(31):13200–13212
- Flenner E, Szamel G (2013) Dynamic heterogeneities above and below the mode-coupling temperature: evidence of a dynamic crossover *J Chem Phys* 138:12A523
- Goldstein M (1969) Viscous liquids and the glass transition: a potential energy barrier picture. *J Chem Phys* 51:3728–3739
- Götze W (2009) Complex dynamics of glass-forming liquids: a mode-coupling theory. Oxford University Press, Oxford
- Harrowell P (2011) The length scales of dynamic heterogeneity: results from molecular dynamics simulations. In: Berthier L, Biroli G, Bouchaud J-P, Cipelletti L, van Saarloos W (eds) (2011) Dynamical heterogeneities in glasses, colloids, and granular media. Oxford University Press, Oxford
- Kauzmann AW (1948) The nature of the glassy state and the behavior of liquids at low temperatures. *Chem Rev* 43:219
- Kirkpatrick TR, Thirumalai D (1987) Dynamics of the structural glass transition and the -Spin-Interaction Spin-Glass Model. *Phys Rev Lett* 58:2091
- Kirkpatrick TR, Wolynes PG (1987) Connections between some kinetic and equilibrium theories of the glass transition. *Phys Rev A* 35:3072
- Kob W (1999) Computer simulations of supercooled liquids and glasses. *J Phys Condens Matter* 11:R85

- Li G, Du MN, Chen XC, Cummins HZ, Tao NJ (1992) Testing mode-coupling predictions for  $\alpha$  and  $\beta$  relaxation in  $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$  near the liquid-glass transition by light scattering. *Phys Rev A* 45(6):3867
- Lunkenheimer P, Kohler M, Kastner S, Loidl A (2012) Dielectric spectroscopy of glassy dynamics. In: Wolynes PG, Lubchenko V (eds) *Structural glasses and supercooled liquids: theory, experiment, and applications*. Wiley, Hoboken
- Mezard M, Parisi G (2012) Glasses and replicas. In: Wolynes PG, Lubchenko V (eds) (2012) *Structural glasses and supercooled liquids: theory, experiment, and applications*. Wiley, Hoboken
- Mezard M, Parisi G, Virasoro M (1988) Spin glass theory and beyond. World Scientific, Singapore
- Richert R (2012) Supercooled liquid dynamics: advances and challenges. In: Wolynes PG, Lubchenko V (eds) *Structural glasses and supercooled liquids: theory, experiment, and applications*. Wiley, Hoboken
- Ritort F, Sollich P (2003) Glassy dynamics of kinetically constrained models. *Adv Phys* 52: 219–342
- Rizzo T (2014) Long-wavelength fluctuations lead to a model of the glass crossover. *EPL* 106:56003
- Rizzo T, Voigtmann T (2015) Qualitative features at the glass crossover. *EPL* 111:56008
- Rizzo T (2016) Dynamical Landau theory of the glass crossover. *Phys Rev B* 94:014202
- Wolynes PG, Lubchenko V (eds) (2012) *Structural glasses and supercooled liquids: theory, experiment, and applications*. Wiley, Hoboken