

Contents

Introduction	4
1 Phenomenological aspects of glassy systems	12
1.1 The glass transition	13
1.2 Strong and fragile glasses	15
1.3 The Kauzmann paradox	17
1.4 Two step relaxation	20
1.5 Glassy behaviour in colloidal suspensions	21
2 Mode Coupling Theory	25
2.1 The basic equations of the Mode Coupling Theory	26
2.1.1 Schematic models	28
2.2 Main results of MCT	29
2.3 Comparison with the experimental data for fragile glasses and colloidal suspensions	32
3 Spin glass models	36
3.1 Spin glass models	37
3.1.1 Edwards-Anderson model	37
3.1.2 Mean-field approximation: SK model	39
3.1.3 p spin model	40
3.2 Replica theory	40
3.2.1 Replica symmetric solution	43
3.2.2 Replica symmetry breaking	44
3.2.3 Physical meaning of the replica symmetry breaking	48
3.2.4 Summary on the replica theory	51

3.3	TAP approach	52
3.4	Langevin relaxation dynamics	56
3.4.1	High temperature equilibrium dynamics	58
3.4.2	Low temperature nonequilibrium dynamics	60
3.5	Link between statics and the dynamics	64
3.5.1	Classification of complex systems	66
4	Spherical version of the frustrated Blume-Emery-Griffiths model	68
4.1	Definition of the spherical frustrated BEG model	71
4.2	Equilibrium properties	72
4.2.1	Saddle point equation	72
4.2.2	Free energy and related quantities for the case $K = 0$	75
4.2.3	Thermodynamics for $K > 0$	81
4.3	Langevin dynamics	81
4.4	Dynamics in the case $K = 0$	84
4.4.1	Dynamics in the nonglassy phase	86
4.4.2	Nonequilibrium dynamics in the glassy phase	90
4.5	Dynamics in the case $K > 0$	92
	Conclusions	98
A	The projection operator formalism	101
B	Derivation of the mode coupling theory	106
B.1	Original derivation	106
B.1.1	Mode coupling approximation	107
B.2	Alternative derivation	109
C	Study of TAP states for the spherical p spin model	114
D	Study of the dynamical equations for the spherical p spin model	119
D.1	Derivation of the dynamical equations	119
D.2	High temperature equilibrium dynamics	122
D.2.1	Two step relaxation	124
D.3	Low temperature nonequilibrium dynamics	125

D.3.1	Long time solution of the dynamical equations	125
D.3.2	Two step relaxation in the presence of aging	127

E	Solution of the dynamics for the spherical frustrated BEG model in the case $K = 0$	129
E.0.3	Study of the equilibrium saddle point equation	130
E.0.4	Computing the function Γ and the density	131

Introduction

The understanding of complex systems is one of the most exciting challenges of the modern theoretical physics. A very important subject of the research in this area is the study of glasses: amorphous solids, i.e. without crystalline order [1, 2, 3, 4, 5, 6, 7]. The common way to produce a glass is by cooling a liquid quickly enough to avoid its crystallization. As the temperature decreases, the continuous increase of viscosity results in a progressive freezing of the liquid, until, at sufficiently low temperatures, the system appears as a disordered solid. Despite this process is well known from a long time, the underlying mechanisms for which a liquid becomes a glass are still in discussion. The precise nature of the glass state is also unclear. Does there exist an independent state of matter which is the glass state? Does it exist as a long-lived metastable state of the matter? Nobody knows the rigorous mathematical answer to these questions. Actually much simpler related questions are unanswered or have taken many efforts to solve. The absence of a simple symmetry group, which is a defining property of the glass state, forbids the use of all the standard solid state techniques, so that first principle computations become very difficult in this case [8].

In the last years the interest about glassy systems is increasing a lot. One of the reasons is that they are largely diffused in ordinary life and offer many important applications. The common glass is a mixture of oxides; other good glass formers are typically amorphous silica, metals and metallic alloys, polymers, organic compounds. However, experiments and computer simulations show that almost any liquid becomes a glass if the cooling rate is high enough. Thus the glass formation should be not a distinguishing property of some materials, but rather a universal one spread out over a wide spectrum of experimental time scales. The great interest around glassy systems is also related

to the fact that these ones can be considered as the archetype of complex systems. Thus the theoretical framework used to describe the glassy phase, the techniques recently developed, could be transferred to many other fields where complex systems are involved, at first sight very far one from another, such as biological systems, vortices in superconductors, granular materials, optimization problems and many others.

Experimentally, the glass transition corresponds to a dramatic slowing down of the dynamical processes. The glass temperature T_g is conventionally defined as the one at which the relaxation time of the liquid becomes of the order of 10^3 seconds or the viscosity reaches 10^{13} poise. This basically corresponds to the temperature for which the relaxation time becomes comparable with the experimental time scale (set by the cooling rate), at which the liquid falls out of equilibrium. A naive way to explain the slowing down of the dynamics is to postulate the existence of a second order phase transition at some temperature around T_g ; thus the surprising increase of the relaxation time would be just the usual critical slowing down observed at the critical point. Such an explanation, although appealing from a theoretical point of view, suffers the fact that no marked changes are found in the structural and thermodynamical quantities passing from the liquid to the glass state and no diverging characteristic length.

The glass transition should be rather a purely dynamical phenomenon, not related to any singularity of the thermodynamical quantities. This is indeed the interpretation provided by the Mode Coupling Theory, which represents one of the main approaches to the supercooled liquids [21, 22, 23, 24, 25]. Introduced by the seminal works of Bengtzelius, Gotze, Sjolander and of Leutheusser independently [20], and then developed by Gotze and Sjogren in the last years, this dynamical theory offers many predictions on the glass transition that can be tested in experiments or computer simulations. One of the most successful results is the characteristic two step relaxation by which the density correlators relax. The particles are initially trapped into cages formed by the nearest neighbours and the correlation function displays a plateau; only subsequently the cages are broken and the correlation decays to zero. The length of the plateau, i.e. the characteristic relaxation time diverges at a temperature T_d ($> T_g$). As this temperature is approached, however, the theoretical expecta-

tions fail for supercooled liquids; activated processes not taken into account by the theory become important, as will be better clarified below. The theory works very well instead for colloidal suspensions, where the interparticle forces are like those of hard spheres and the activated processes are probably less important.

On the other hand, it was noted by Kauzmann long ago, that a real thermodynamic phase transition could be obtained in the limit of an infinitely slow cooling. This idea was put forward to solve the following paradox. The configurational entropy ΔS is defined experimentally as the entropy difference between liquid and crystal; this quantity behaves smoothly in the supercooled liquid until the system becomes a glass (see Fig. 1.3). When cooled more slowly the system follows the smooth $\Delta S(T)$ curve down to slightly lower temperatures, but then freezes again. If extrapolated $\Delta S(T)$ vanishes at a finite temperature T_K and would be negative below this temperature, with the unpleasant feature that the entropy of the crystal would be lower than the liquid one. Thus, to avoid this paradox a real phase transition is assumed at T_K which would lead to $\Delta S(T) = 0$ for $T < T_K$.

The idea of an underlying ideal phase transition, which could be obtained only at infinitely slow cooling, receives some support from the measurements of the relaxation time. For fragile glasses the experimental data are well fitted by the Vogel-Fulcher law, $\tau = \tau_0 \exp\left(\frac{A}{T-T_{VF}}\right)$, and this would predict a phase transition at a temperature $T_{VF} < T_g$, not accessible experimentally (while staying at equilibrium). Well, the two extrapolated temperatures T_K and T_{VF} turn out to be surprisingly close each other. The first phenomenological attempts to explain this fact originate in the work of Kauzmann [9], then developed by Adam, Gibbs and Di Marzio [10, 11], which identifies the glass transition as a real thermodynamic transition blurred by some dynamical effects.

An indirect route towards structural glasses is given by the study of spin glass models. These systems are composed by simple spins interacting through competing quenched random interactions (quenched stands for time-independent over all the experimental time scales). The intrinsic disorder combined with the competing interactions implies the presence of frustration in these systems, which is the inability that spin configurations satisfy all the interactions simul-

taneously; this important feature lies on the basis of their complex behaviour. Let us notice that in glass forming systems, frustration arises when the irregular shape of molecules or the realization of stable local arrangements, prevents the system from reaching an ordered state; in this case the disorder is not quenched, but rather self-induced by the slow dynamics itself of the particles. Nevertheless, spin glasses bear many similarities with glass forming systems, as concerned experimental and theoretical properties. In the last years several powerful tools have been developed which allow to treat spin glass models in great details, at least at mean field level (infinite range interactions).

Due to the presence of frustration, for low enough temperature the free energy landscape of mean field spin glass models has many valleys, unrelated by a simple symmetry, separated by free energy barriers that grow asymptotically as the size of the system. At equilibrium these models undergo a phase transition at a critical temperature T_c which is well described by a spontaneous replica symmetry breaking scheme [35, 36, 37, 38, 39]. In this framework the order parameter is a function $q(x)$ defined on the interval $[0, 1]$, whose values represent the possible values of the overlap among two valleys. Actually the most pressing analogies with glasses have been noted for a particular class of mean-field spin glass models, the so called 'discontinuous' ones. This name derives from the fact that for these models $q(x)$ changes discontinuously at T_c , although the transition is of second order in the Ehrenfest sense. Another name often found in the literature for these models is 'one step RSB' spin glasses, because of the special pattern of symmetry breaking involved in their solution. Well, one of the remarkable feature of these 'discontinuous' spin glasses, first discovered in [45], is that the equilibrium transition at T_c is associated with an entropy crisis, namely the vanishing of the configurational entropy, as expected in the ideal Kauzmann scenario of glasses.

The study of Langevin dynamics of mean field spin glass models starting from a random initial condition (i.e. instantaneous quench from infinite temperature) reveals other deep connections with complex systems in which the disorder is a priori absent [40, 41, 42]. In the 'discontinuous' models there exists a dynamical transition at a temperature T_d , larger than the equilibrium transition T_c , which is exactly described by the Mode Coupling Theory in its schematic formulation; this important feature was first noticed by Kirck-

patrick, Thirumalai and Wolynes in a series of inspired papers of the mid-eighties [62]. However the existence of a dynamic singularity at a temperature above the true thermodynamic one is possible only at mean field level (due to metastable states of infinite lifetime) and has been conjectured that in realistic systems like a glass, the region between T_c and T_g has instead a finite, but very rapidly increasing relaxation time (see Fig. 2.2).

In the low temperature phase of mean field models, for $T < T_d$, the equilibrium is never achieved, the system is no longer stationary but exhibits a slow dynamics which depends on the whole history of the system up to the beginning of its observation. Schematically, new relaxation processes come into play on a time scale comparable to the age of the system: the older the system, the longer the time needed for this 'aging' relaxation to take place. These effects are well known from some nonequilibrium experimental observations, namely the slow relaxations and the aging phenomena which are observed for real spin glasses and many other glassy systems [40]. Recent years have seen important developments on the study of the out of equilibrium dynamics of the glassy phases, initiated by the exact solution of the dynamics in a discontinuous spin glass model by Cugliandolo and Kurchan [68]. It has become clear that, in realistic systems with short range interactions, the pattern of replica symmetry breaking can be deduced from the measurements of the violation of the fluctuation-dissipation theorem [73, 74].

A class of widely studied experimental systems, which displays a large variety of kinetic phenomena having many connections with the glass transition, is given by the colloidal suspensions [13, 14, 15]. These systems can be prepared for a large span of densities, and the interaction can be tuned to some extent by varying the coating of the particles and the composition of the solvent. It is possible to realize an hard-sphere system, the basic model underlying all theories of simple liquids [19]. By the addition of polymer, one can also prepare systems where the hard core is complemented by an attractive shell; this allows to study the interplay of repulsion and attraction. Equilibrium phase diagrams in the plane temperature - volume fraction show transitions between gas, liquid and solid phases. However these predictions are not always realized in practice; rather systems exhibit a rich nonequilibrium phenomenology. They often become undercooled, supersaturated, or trapped in gel-like or glass states. In

many cases the products strongly depend on the starting position in the phase diagram and discrepancies between predictions and actual observations are due to the intricacies of the dynamics.

Of course, the above picture offered by mean field spin glass models cannot be taken as completely satisfactory. Despite the cited resemblances, these models are microscopically quite different from glass forming systems and thus not suitable to their description. Apart the mean field character and the presence of quenched disorder, they do not contain particles; so as an example they do not allow to describe the molecular motion of a supercooled liquid, or that of suspended colloidal particles. As shown above, moreover, many systems behave quite differently according to structural parameters determined by the experimental conditions; in order to get a unifying description of these systems it is crucial to understand the interplay between the density and the other parameters.

Recently, to make stronger connections with physical systems, some models have been introduced which combine features of spin glasses and lattice gas. Being constituted of particles, they allow to introduce the density and other related quantities which are usually important in the study of liquids. In this thesis we consider the frustrated Blume-Emery-Griffiths (BEG) model [80], which is a quite general framework to describe different complex systems. Essentially the model consists of a lattice gas ($n_i = 0, 1$) in a frustrated medium where the particles have an internal degree of freedom, given by their spin ($s_i = \pm 1$), which may account, as an example, of the possible orientations of complex molecules in glass forming systems. Since the presence of frustration in the model, two particles can be nearest neighbours only if the relative orientation is appropriate, otherwise they have to move apart; frustrated loops correspond in the liquid to those loops which, due to geometric hindrance, cannot be fully occupied by the particles. These steric effects are greatly responsible for the geometric frustration appearing in glass forming systems at low temperatures or high densities; thus the model offers a clear and intuitive picture of the mechanism leading to a glass transition, qualitatively reproducing the complex dynamical behaviour present in this regime. Moreover, the particles interact also through a potential depending on the coupling K , which allow to implement possibly a further attractive component, besides the hard

core one, as occurs in the colloidal suspensions with addition of polymers.

A complete mean-field solution of the equilibrium properties has been found only recently in [81], by solving numerically the equations of the full replica symmetry breaking scheme using a suitable technique of integration; moreover a dynamical treatment of the model is still lacking. Then we introduce a suitable spherical version of the BEG model which allows a complete analysis of its equilibrium and dynamical properties [82]. Compared with the Ising case, this spherical version is less frustrated and the spin glass phase is described by a single-valued order parameter i.e. by a replica symmetric solution; however the advantage is to allow for a full analytical treatment. Furthermore, the description of the model in terms of continuous lattice fields allows us to implement the Langevin dynamics; thus we can investigate the time evolution of the various correlation and response functions and of density. The model is characterized by a large variety of behaviours obtained by varying its parameters; the overall qualitative picture is similar to that evidenced by the physical systems indicated previously. For K positive the phase diagram in the plane density - temperature shows the existence of a tricritical point which connects two kinds of transition lines (see Fig. 4.3). At that located below the tricritical point, the order parameters (overlap and density) discontinuously jump and a first order transition takes place with coexistence of the liquid and glassy phase. In the same region the analysis of the dynamics displays the existence of a dynamical transition line, different from the static one, depending on the initial density. Still in the liquid phase, but very close to this critical line, we have also put in evidence the existence of the interrupted aging effect due to a large but finite equilibration time; from an experimental or numerical point of view, this effect could make rather ambiguous the onset of the glassy phase if the system is probed on restricted time windows. The other line connected to the tricritical point, is a glass transition line where the density does not jump and the equilibrium correlation functions display a diverging relaxation time. This scenario is similar to that evidenced by recent studies on the Mode Coupling Theory for a square-well-system (hard core particle repulsion plus attractive potential), which have led to postulate the existence of so-called 'attractive glasses' at density values well below that predicted by the hard sphere system [33, 34]. The model can be taken as the starting point for fu-

ture qualitative and quantitative improvements or extensions to other complex systems.

Outline of the thesis

The thesis is organized as follows. In Chapter 1 we describe some phenomenological aspects of the glass transition and glass forming systems. In Chapter 2 we present the mode coupling theory, specifically its basic equations, results, and the comparison with the experimental data for several kinds of glassy systems. In Chapter 3 we study the spin glass models at mean field level illustrating the various basic techniques. In Chapter 4 we introduce the spherical frustrated Blume-Emery-Griffiths model and study its equilibrium and dynamical properties.

Moreover, several appendices contain further investigations of the various issues, which need a more involved technical analysis. A detailed introduction on the Mori-Zwanzig projector formalism is given in Appendix A. In Appendix B the conventional derivation of the Mode Coupling Theory is carried out, based on the Mori-Zwanzig projector formalism; an alternative more transparent derivation recently developed is also briefly presented. In Appendix C we study the TAP states of the spherical p spin glass model and in Appendix D its dynamical equations for both the low and high temperature phase. Finally, in Appendix E we present in detail the dynamical solution of the spherical frustrated Blume-Emery-Griffiths model in the case of zero particle-particle coupling ($K = 0$).

Chapter 1

Phenomenological aspects of glassy systems

In this chapter we describe the main phenomenological properties which characterize glass forming systems [1, 2, 3, 4, 5, 6, 7]. The glass transition essentially consists in a solidification without crystallization. It is observed in a large variety of substances like covalently bonded systems like SiO_2 , hydrogen-bonded liquids, ionic mixtures, polymers, molecular van der Waals liquids. However, experiments and computer simulations suggest that almost any liquid becomes a glass if the cooling rate is high enough. When a glass former is cooled from its melting temperature to the glass transition temperature, it shows an increase of the relaxation time by many decades without a significant change in its structural properties. The set of phenomena observed during this process should be due only to a dynamical transition, without any singularity in the thermodynamical quantities; on the other hand the Kauzmann paradox gives some evidence that a real thermodynamic phase transition could exist in the limit of an infinitely slow cooling. However, a theory able to explain just the salient phenomenology is still lacking.

Colloidal suspensions display a large variety of kinetic phenomena, having many interesting connections with the glass transition [13, 14, 15]. They can be prepared for a large span of densities, and the interaction can be tuned in order to realize an hard-sphere system, or systems where the hard core is complemented by an attractive shell. A rich nonequilibrium phenomenology

is exhibited; systems often become undercooled, supersaturated, or trapped in gel-like or glass states. Colloid science aims to understand the underlying mechanisms of these transitions.

1.1 The glass transition

The classical way to produce glass is to cool a liquid quickly enough that crystallization has no time to occur. As the temperature decreases the continuous increase of viscosity results in a progressive slowing down of the molecular dynamics, until, at sufficiently low temperature, the system cannot equilibrate anymore on the time scale set by the cooling rate and appears as a disordered solid, commonly called glass.

Different from the gaseous, liquid and crystalline solid state of matter, the glassy state has been thought to be reserved for a particular class of materials, the glass formers [2]. Many experiments have been realized to search for new members of this family and to understand by which mechanisms some materials form glass and others do not. Traditional cooling rates in good glass formers like window glass are typically of order $10^{-2} K s^{-1}$. Based on the experience made on this time scale, metals and alloys were for a long time considered as non glass forming systems. By using new techniques, however, cooling rates of order $10^{-5} K s^{-1}$ and higher could be achieved, at which many metallic alloys form glasses. A further extension of the family of glass forming systems can be realized by considering the results of computer simulations: in fact it has been found that at cooling rates of order $10^{-12} K s^{-1}$ simple liquids, like liquid argon (to all appearances one of the worst candidates for glass formation), exhibit a broad transition which resembles a glass transition. These results suggest that glass formation is not a distinguishing property of materials, but rather a universal one spread out over a very wide spectrum of experimental time scales. This is not surprising since glass formation is solidification without crystallization, and then the ability to form a glass strongly depends on the time necessary to crystallization and on the possibility to avoid it during the cooling.

Let us consider the behaviour of the specific volume at constant pressure as a function of the temperature during the process of cooling [7]; it is schemat-

ically represented in Fig. 1.1. If the cooling is slow the liquid undergoes the crystallization at the melting temperature T_m and the specific volume discontinuously jumps at this temperature. Instead, when the liquid is quenched quickly enough to avoid the crystallization, the specific volume displays no discontinuity at the melting temperature T_m , but decreases with the same slope of the liquid; the system is called a supercooled liquid. Then, in a narrow interval around a temperature T_g , the slope of the curve changes very quickly but continuously, so to become close to that of the crystalline solid. In this narrow interval we have thus the passage to the glass state. The specific heat behaves in an analogous way (see Fig. 1.1). Actually no discontinuity occurs in any physical quantities but only a rapid change on passing through T_g . Thus, the above behaviour does not correspond to a true thermodynamical phase transition. It should be more appropriate to speak of a crossover of some physical quantities that would correspond to a transition of dynamical nature, due to purely kinetic effects.

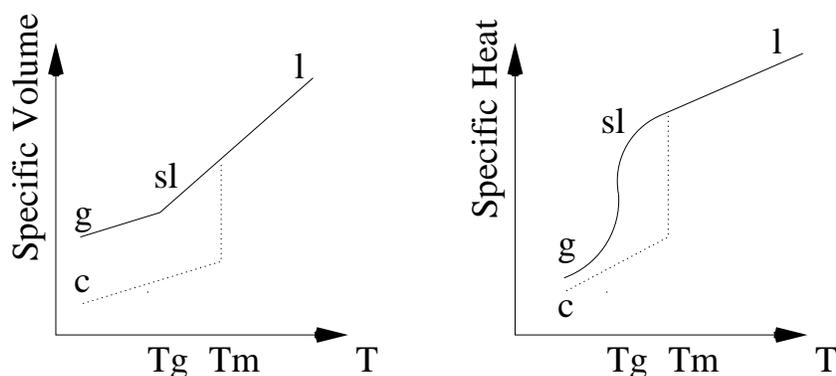


Figure 1.1: Schematic representation of the specific volume and of the specific heat as a function of temperature (l: liquid; sl: supercooled liquid; c: crystal; g: glass)

The transition temperature T_g , called glass temperature, is conventionally defined as the one at which the typical structural relaxation time τ of the liquid becomes of the order of 10^3 seconds, or equivalently, the viscosity is about 10^{13} poise. This basically corresponds to the temperature for which the relaxation time becomes comparable with the experimental time scale (set by the cooling rate $\Gamma = -dT/dt$), at which the liquid falls out of equilibrium (i.e. $T_g \simeq \tau\Gamma$).

The purely dynamical character of the glass transition is confirmed by the experimental observation that the glass temperature T_g depends on the cooling rate and the properties of the glasses depend on their history of preparation. Actually, T_g decreases slightly when Γ decreases: the slower is the cooling, the longer is the time the liquid has to thermalize in the allowed configurations, so it can reach a lower temperature before falling out of equilibrium and this leads to a lower T_g . The dependence of T_g from the cooling rate Γ is well approximated by a logarithmic law and in practice is weak: only a few K when Γ changes for an order-of-magnitude. Thus T_g can be almost considered as a property of the material.

It should be appealing to associate the huge increase of the relaxation time with a standard second order phase transition at some temperature around T_g ; then the slowing down could be explained as the usual critical slowing down observed at the critical point. However no growth of a structural correlation length has been detected so far in supercooled liquids. Quite to the contrary, the variations of structure in liquids and glasses, as measured in neutron and X-ray diffraction experiments, appear rather bland [4]. The ordinary high temperature liquid has only short range order whose signature in the static structure factor is a broad peak (or a split peak for some molecular systems) at a given wave vector that roughly corresponds in real space to some typical mean distance between neighbouring molecules. As the temperature is lowered and the supercooled regime is entered, there are small continuous variations of the structure factor that mostly reflect the change in density (typically a 5% change between T_m and T_g) and, possibly, some adjustments in the local arrangements of the molecules. There is no sign, however, of a significantly growing correlation length.

1.2 Strong and fragile glasses

The characteristic relaxation time τ can change by many orders of magnitude for small variations of temperature during the cooling process. The same behaviour is found for the viscosity η , which can be related to τ via the Maxwell relation, $\eta = G_\infty \tau$, where G_∞ is the infinite frequency shear modulus. Such a dramatic variation of the relaxation time as a function of the temperature

has been represented by Angell [5]; his plot of $\log \eta$ versus T_g/T allows to distinguish several types of behaviour (see Fig. 1.2). So called strong glasses,

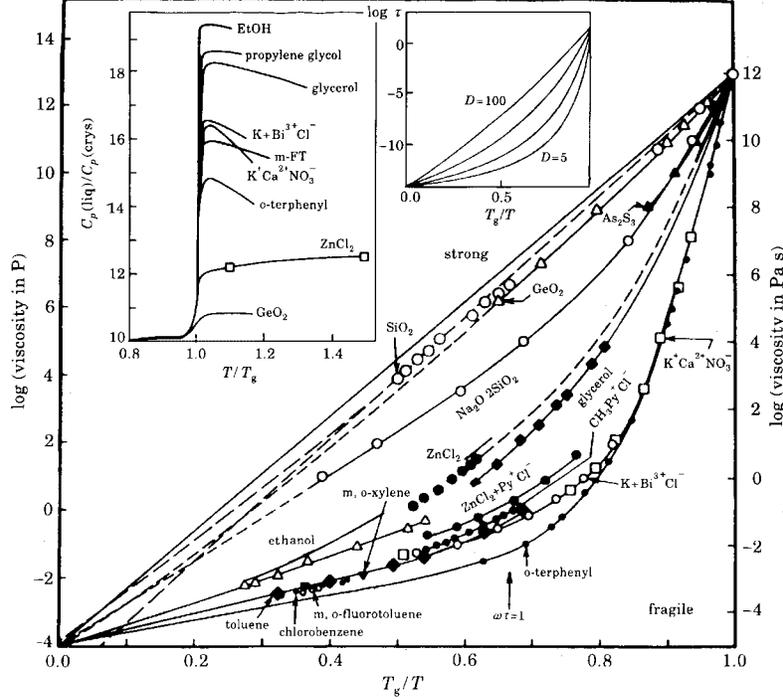


Figure 1.2: Main figure: Viscosity of different glass-formers as a function of T_g/T , where T_g is the glass transition temperature. For GeO_2 , a system forming a network of strong intermolecular bonds, the variation is almost linear, whereas the other liquid (glycerol, m-toluidine and orthoterphenyl) are characterized by a strong departure from linear dependence. Left inset: Temperature dependence of the specific heat, normalized to its value for the crystal, for different glass-formers. .

which form 2- or 3- dimensional networks of strong bonds (like SiO_2 and GeO_2), show an Arrhenius behaviour between T_g and the high temperature region, described by

$$\tau = \tau_0 \exp\left(\frac{\Delta F}{k_B T}\right) \quad (1.1)$$

(linear shape in the plot in Fig. 1.2) where ΔF is the typical free energy barrier or the effective activation free energy. On the other hand, other glasses called fragile glasses, that are the vast majority, are characterized by a non-Arrhenius behaviour; in this case the increase of the relaxation time when decreasing

temperatures is much faster than the Arrhenius one (marked upward curvature in Fig. 1.2). Thus the typical free energy barrier increases when T decreases. This is indicative of thermally activated dynamics and implies a collective behaviour involving more and more particles. In this case the relaxation time versus temperature is well fitted by the Volger-Fulcher law

$$\tau = \tau_0 \exp \left[\frac{A}{k_B (T - T_{VF})} \right] \quad (1.2)$$

which would predict a phase transition at a temperature T_{VF} which is not accessible experimentally (while staying at equilibrium). The more fragile the glass, the closer is T_{VF} to T_g , while strong glasses have a T_{VF} close to zero. There are, however, alternative fitting formulas that have been also used, some of which do not imply any singularity at a nonzero temperature.

The above described dramatic increase of the relaxation time or the large typical free energy barrier is a peculiar feature of glass phenomenology and is not commonly encountered. For instance in the field of standard critical phenomena, the slowing down of the dynamics occurring when approaching the critical point is usually characterized by a power law growth of the relaxation time and not by an exponential growth.

1.3 The Kauzmann paradox

We have seen previously that despite some similarities, it is not possible to classify the passage to the glass state as a thermodynamic transition, since the glass temperature T_g depends on the time scale set by the cooling rate and no marked changes are found in the thermodynamical and structural quantities. Actually, from the experimental data no true thermodynamic transition is ever directly observed since the system falls out of equilibrium before it could happen. The Kauzmann paradox which now describe and the experimental observation that at low cooling rate the glass transition is much sharper, have suggested the possibility that a thermodynamic phase transition appears in the limit of infinitely slow cooling rate and this ideal glass transition underlies the real glass transition occurring at finite rates.

Below the melting point T_m the specific heat of a supercooled liquid is larger than that of the corresponding crystal (see Figs. 1.1 and 1.2); as a con-

sequence of this excess specific heat, the entropy difference between the liquid and the crystal, which is an experimental measure of the so called configurational entropy ΔS , decreases with temperature, typically by a factor 3 between T_m and T_g for fragile liquids, until the system becomes a glass. When cooled more slowly the system follows the smooth $\Delta S(T)$ curve down to slightly lower temperatures, but then freezes again. If extrapolated $\Delta S(T)$ vanishes at a finite temperature T_K and would be negative below this temperature, with the unpleasant feature that the entropy of the crystal would be lower than the liquid 1.3. Thus, to avoid this paradox one can admit that for an infinitely slow cooling ΔS vanishes at T_K and remains zero for temperature $T < T_K$. Since the liquid can now reach the equilibrium at all the temperatures, this would mean that at T_K there is a real thermodynamic phase transition for the supercooled liquid.

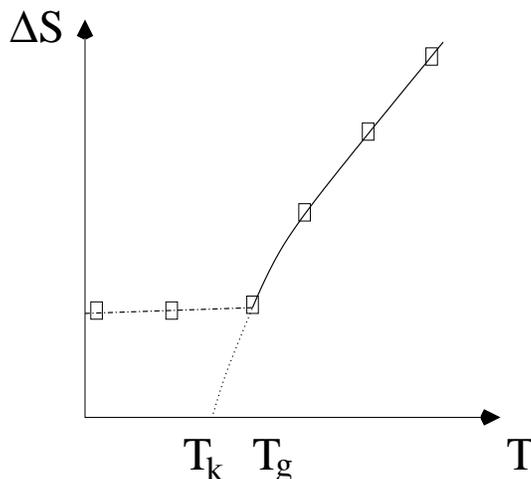


Figure 1.3: Configurational entropy ΔS as a function of the temperature. The squares indicate the experimental points. The full line is a fit of the equilibrated data and the dotted line is an extrapolation of their behaviour below T_g .

However this is of course not the only possibility to solve the Kauzmann paradox. For example one can suppose that the extrapolation for infinitely slow cooling is not valid and that the real equilibrium $\Delta S(T)$ curve is a smooth function of the temperature which vanishes gradually at $T = 0$, as it does in the Debye theory of crystals.

This idea of an underlying ideal phase transition, which could be obtained only at infinitely slow cooling, is supported from the following observation: the two temperatures where the extrapolated experimental behaviour has a singularity, T_{VF} and T_K , turn out to be surprisingly close to each other, as can be seen from the table below (taken from [6]). The first phenomenological attempts to explain this fact originate in the work of Kauzmann [9], and developed by Adam, Gibbs and Di Marzio, which identifies the glass transition as a true thermodynamic transition blurred by some dynamical effects [10, 11].

In the Adam-Gibbs picture, the relaxation takes place by increasingly cooperative rearrangements of groups of molecules, which relax independently one from another. The effective activated energy goes as the inverse of the configurational entropy and if this quantity is identified as the entropy difference between the supercooled liquid and the crystal, then the theory allows to correlate the extrapolated divergence of the relaxation time with the Kauzmann paradox [10]; in particular a linear behaviour of $\Delta S(T)$ implies the Volger-Fulcher law. The vanishing of the configurational entropy at a nonzero temperature is also predicted in the Gibbs-Di Marzio approximate mean field treatment of a lattice model of linear polymeric chains [11].

The free energy landscape described by the Adam-Gibbs scenario can be imagined as an incredibly complex multi-dimensional set of hills, valleys, basins, saddle points and passage-ways around the hills. However, the fraction of space which is accessible to the representative state point of the system decreases with decreasing temperature, and the system becomes constrained to deeper and deeper wells. At low enough temperature, when the representative point of the supercooled liquid is mostly found in fairly deep and narrow wells, it seems reasonable to define a 'configurational entropy', that is proportional to the logarithm of the number of minima that are accessible at a given temperature. The liquid configurations corresponding to these accessible minima have been called 'inherent structures' and Stillinger and coworkers have recently designed a gradient-descent mapping procedure to find the inherent structures and study their properties in computer simulations [88].

Actually, the problem of the existence of a true thermodynamic transition at $T_K = T_{VF}$ is still unsolved; in the discontinuous mean field spin glass models with quenched disorder, such transition exists and is of a strange type. It is of

second order because the entropy and internal energy are continuous; on the other hand the order parameter is discontinuous at the transition. Let us note that the individuation of an order parameter in real glass forming systems is not obvious. It can be identified as the modulation of the microscopic density profile (for a more precise definition see [8]) and also displays a discontinuous character at the transition, i.e. as the system freezes there is a finite jump in this modulation.

Substance	$T_K (K)$	$T_{VF} (K)$	$T_g (K)$
o-therphenyl	204.2	202.4	246
salol	175.2		220
2-MTHF	69.3	69.6	91
n-propanol	72.2	70.2	97
3-bromopentane	82.5	82.9	108

(1.3)

1.4 Two step relaxation

In an ordinary liquid above the melting point, relaxation functions are usually well described, after some transient time, by a simple exponential decay. One of the peculiar features of glass forming systems is the appearance, already at temperature higher than the glass transition temperature T_g , of dynamical anomalies. Johari and Goldstein, by studying the relaxation spectrum of fragile glass formers by dielectric spectroscopy techniques [12], observed that at sufficiently low temperatures, but higher than T_g , the relaxation spectrum presents two peaks: the high frequency (low time) peak, which is interpretable as corresponding to the motion of particles within the cage formed by their nearest neighbours (called β -relaxation), and the high frequency (short time) one corresponding to the more cooperative motion for which the particles escape their initial cages (called structural or α -relaxation). When the relaxation function is plotted against the logarithm of the time, one observes what is called a 'two step relaxation' (see Fig. 2.1) .

The analysis of experimental data has shown that the long time relaxation is nonexponential, but well fitted by a stretched exponential, also called

Kohlrausch-Williams-Watts function:

$$\Phi(t) = A \exp \left[- (t/\tau)^\delta \right] \quad (1.4)$$

This form of decay can be interpreted as the result of many processes, occurring over different time scales. Instead power laws are used to reproduce the relaxation function in the in range of intermediate times. The Mode Coupling Theory that we present in the next chapter, is able to predict the dynamical behaviour now described.

1.5 Glassy behaviour in colloidal suspensions

A class of systems which displays a large variety of kinetic phenomena, having interesting connections with the glass transition, is given by the colloidal suspensions. They have been studied extensively because their practical importance and their relevance in biophysics. These systems are also of great theoretical interest since they are models for conventional matter. They can be prepared for a large span of densities, and the interaction can be tuned to some extent by varying the coating of the particles and the composition of the solvent. It is possible to realize an hard-sphere system, the basic model underlying all theories of simple liquids. One can also prepare systems where the hard core is complemented by an attractive shell; this allows to study the interplay of repulsion and attraction. Fig. 1.4 illustrates the possible types of phase diagrams that are expected at equilibrium, in the plane temperature - volume fraction. However the predictions of equilibrium phase diagrams are not always realized; rather systems exhibit a rich nonequilibrium phenomenology. They often become undercooled, supersaturated, or trapped in gel-like or glass states. In many cases the products strongly depend on the starting position in the phase diagram and discrepancies between predictions and actual observations are due to the intricacies of the dynamics of phase transitions.

Hard sphere colloids suspended in a solvent provide the simplest illustration of the subtleties involved. In this case the phase diagram is a straightforward crystal-fluid equilibrium. Entropy considerations predict that these systems form crystals if the volume fraction is increased. Above the 'freezing' volume

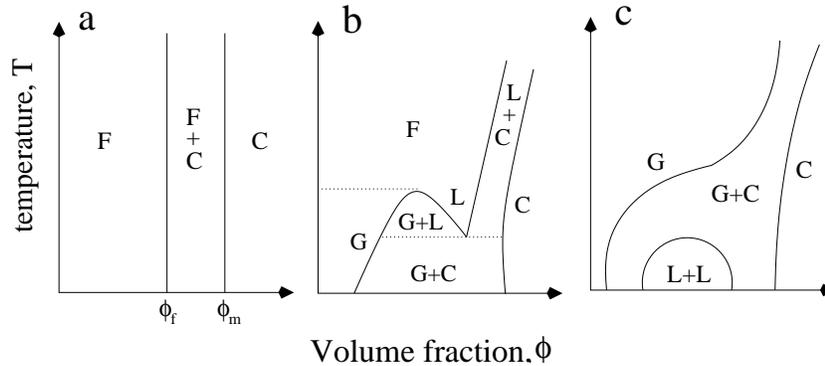


Figure 1.4: A wide range of phase diagrams occurs naturally [15]. **a)** for a purely hard sphere system the phase diagram shows only fluid (F) and crystal (C) phases. **b)** Atomic systems are often modelled by hard sphere systems with long range attractions. This leads to equilibrium between gas (G), liquid (L) and crystal phases. **c)** In cases where the attraction is short range, as in protein systems, equilibrium between gas and crystal is found, but the liquid-liquid transition becomes metastable.

fraction, $\phi_f = 0.494$, it is entropically favourable if some spheres are in a crystal, but above the 'melting' volume fraction, $\phi_m = 0.545$, all spheres should be in a crystal (Fig. 1.4a). Instead Pusey and van Megen [30] clearly observed that above a certain volume fraction ($\phi_g = 0.58$) an amorphous glassy phase appeared that did not crystallize over several months. The value $\phi_g = 0.58$ is not an intrinsic glass transition volume factor for hard sphere colloidal suspensions; recently samples with high volume fractions, which fail to crystallize even after a year on Earth, have been seen to crystallize fully in less than two weeks in microgravity ($10^{-6}g$). This have also been corroborated in experiments on centrifuged samples and indicates that even a small amount of uniaxial stress can jam a system such that crystallization is not observed.

The addition of nonadsorbing polymers is able to produce an attraction between the colloidal particles. The first theoretical interpretation of this polymer-induced attraction was due to Asakura and Oosawa [18], who discussed it in terms of the 'depletion' effect. Colloids are surrounded by a depletion zone from which the polymers are sterically excluded. When the colloids are close enough there is an overlap of depletion zones, causing an unbalanced osmotic pressure pushing the particles together, which can be expressed as an attractive pair potential. An advantage of such systems is that the range

and the depth of the potential are controlled by the size and volume fraction of the polymer respectively. Depending on the relative sizes of the polymer and the colloid, two distinct situations can be resolved (see Fig. 1.5a,b); not only the gas-crystal coexistence described above is exhibited, but also gas, liquid and crystal coexistence. Note that the polymer concentration goes as the inverse temperature, thus Figs. 1.5a,b correspond respectively to Figs. 1.4b,c. Although it is possible to predict the equilibrium phases of such systems, they also show a frustrating behaviour. Fig. 1.5c shows as the crystal phase predicted at equilibrium is reached only in a narrow window close to the phase boundary. Eventually deep in the phase diagram, due to various aggregation mechanisms, the system is trapped in a gel-like state instead. Much depends on the initial conditions, in this case polymer concentration and colloid volume fraction. Although slightly changing one condition may not alter which equilibrium phase is expected, it may significantly affect whether or not they are reached. Predictions of the kinetics often come from free energy diagrams, from which the unstable and metastable regions and the common associated mechanisms of spinodal decomposition, nucleation and growth are delineated. Furthermore, glass states can be obtained also in this case. Non-equilibrium phenomena characterized by intriguing aspects have been recently found, which cannot be understood from the glass states formed in hard sphere solutions; these will be discussed in the next chapter. Mode Coupling Theory has played a leading role in colloidal systems, interpreting and rationalizing some of the observations and achieving quite acceptable numerical agreement in comparison to experiments.

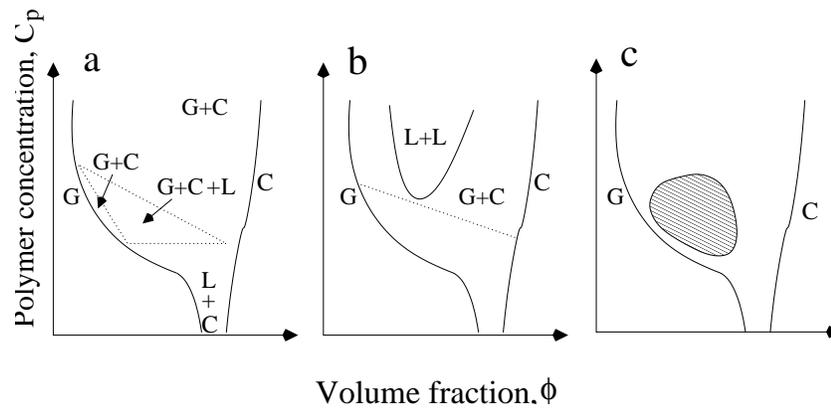


Figure 1.5: Phase diagrams indicating coexisting phases, similar to those of Fig. 1.4 but inverted, as polymer concentration plays the role of inverse temperature. **a)** (large polymer) is similar to an atomic system, having regions of three phase equilibria. **b)** (small polymer) is similar to systems found for some proteins, with two-phase coexistence and a metastable liquid-liquid region. **c)** The situation often found experimentally for short polymers. The shaded area indicates the region where aggregation occurs; only in the narrow region close to the phase boundary are the equilibrium phases reached.

Chapter 2

Mode Coupling Theory

Mode Coupling Theory (MCT) is one of the main theoretical approaches to the supercooled liquids near the glass transition [21, 22, 23, 24, 25]. It puts forward the idea that at low temperatures the nonlinear feedback mechanisms in the microscopic dynamics of the particles become so strong to lead to the structural arrest of the system. The glass transition at the critical temperature T_d corresponds to a singularity exhibited by the solutions of the equations of motion for the density autocorrelation functions, the so called mode-coupling equations, obtained through some suitable approximations from the canonical equations of motion.

For temperature higher than T_d the theory predicts most of the peculiar behaviours which are observed for fragile glass formers; however very close to T_d the theoretical expectations are no more in agreement with the experimental data, since activated processes, not taken into account by MCT, become important. On the other hand the theory works very well for colloidal suspensions, where the interparticle forces are like those of hard spheres and the activated processes are probably less important [32]. When the inter-particle potential contains an attractive part, besides the repulsive hard-core two intersecting liquid-glass transition lines appear, one which extends to low densities, while the other one, at high densities, shows a re-entrant behaviour [33]. These results have had some evidence by recent experiments [34].

2.1 The basic equations of the Mode Coupling Theory

The dynamics of liquids is usually described by means of correlation functions of the density fluctuation modes [19]. One of the basic quantity is the intermediate scattering function, defined as

$$S_{\mathbf{q}}(t) = \frac{\langle \delta\rho_{\mathbf{q}}^* \delta\rho_{\mathbf{q}}(t) \rangle}{N} \quad \rho_{\mathbf{q}}(t) = \sum_{i=1}^N \exp(i\mathbf{q} \cdot \mathbf{r}_i(t)) \quad (2.1)$$

where N is the number of particles, $\mathbf{r}_i(t)$ the position of the particle i at time t and $\langle \rangle$ the Boltzmann average. The $t = 0$ value of $S_{\mathbf{q}}(t)$ determines the static structure factor, $S_{\mathbf{q}} = \langle \delta\rho_{\mathbf{q}}^* \delta\rho_{\mathbf{q}} \rangle / N = (\langle \rho_{\mathbf{q}}^* \rho_{\mathbf{q}} \rangle - N^2 \delta_{\mathbf{q},\mathbf{0}}) / N$, while its Fourier transform defines the dynamical structure factor, $S_{\mathbf{q}}(\omega)$, which is directly measurable by neutron or light scattering experiments. One can then introduce the correlator $\Phi_{\mathbf{q}}(t)$, which is the main object in MCT, normalizing the intermediate scattering function by the static structure function:

$$\Phi_{\mathbf{q}}(t) = \frac{S_{\mathbf{q}}(t)}{S_{\mathbf{q}}} = \frac{\langle \delta\rho_{\mathbf{q}}^* \delta\rho_{\mathbf{q}}(t) \rangle}{\langle \delta\rho_{\mathbf{q}}^* \delta\rho_{\mathbf{q}} \rangle} \quad (2.2)$$

The equations of motion for $\Phi_{\mathbf{q}}(t)$ in the case of an isotropic system are written as

$$\ddot{\Phi}_q(t) + \Omega_q^2 \Phi_q + \int_0^t M_q(t-u) \dot{\Phi}_q(u) du = 0 \quad (2.3)$$

where Ω_q is a microscopic frequency related the static structure factor, $\Omega_q^2 = q^2 k_B T / (m S_q)$ (m is the mass of the particles and k_B Boltzmann's constant). One can recognize in (2.3) for a given mode q the equation of motion of a damped harmonic oscillator with the complication of a retarded friction proportional to the kernel $M_q(t)$. We emphasize that, if a special expression for $M_q(t)$ is assumed, the equations of motion (2.3) are exact. They can be obtained by means of the Mori-Zwanzig projection operator formalism (see App. A); the kernel $M_q(t)$ that one finds is given by Eq. (B.6), derived in App. B; the initial conditions are $\Phi_q(0) = 1$, $\dot{\Phi}_q(0) = 0$.

MCT is obtained through the mode coupling approximation (see App. B) for which the kernel $M_q(t)$ is written as sum of a sharply peaked term, $\nu_q \delta(t)$,

and a contribution $\Omega_q^2 m_q(t)$ expressed as a quadratic form of the correlators $\Phi_q(t)$, i.e.

$$M_q^{MCT}(t) = \nu_q \delta(t) + \Omega_q^2 m_q(t) \quad (2.4)$$

$$m_q(t) = \sum_{\mathbf{k}+\mathbf{p}=\mathbf{q}} V(\mathbf{q}, \mathbf{k}, \mathbf{p}) \Phi_k(t) \Phi_p(t) \quad (2.5)$$

where the vertices $V(\mathbf{q}, \mathbf{k}, \mathbf{p})$ are coefficients assumed to depend on the physical control parameters like density or temperature; they are related to the static structure factor S_q (see Eq. (B.17)), which can be obtained experimentally or computed from the pair potentials. With this approximation one arrives therefore to a closed set of coupled equations for the correlators Φ_q , the so called mode-coupling equations, which thus give their full time dependence. These are the equations originally proposed by Bengtzelius, Gotze and Sjolander [20] describing the idealized structural glass transition. The kernel m_q can be extended for convenience to a general polynomial in the variables Φ_q .

The long time behavior of the solutions of the mode coupling equations changes if the vertices pass certain critical values V_c . Beyond this threshold, the correlators do not decay to zero at infinite times. This means that a density fluctuation that was present at time zero does not disappear even at very long times, i.e. the system is no longer ergodic. Solutions for which $\Phi_q(t \rightarrow \infty) = f_q \neq 0$, corresponding to low temperatures and high densities, are interpreted to describe an ideal glass state; the quantity f_q is defined as the non-ergodicity parameter. Instead solutions so that $\Phi_q(t \rightarrow \infty) = 0$ (for each q) correspond to a liquid state. The singularity at V_c , accompanied by a diverging relaxation time, is identified with the idealized glass transition. Note that the vertices are assumed to depend smoothly on the physical control parameters, so the transition observed is due only to the non-linearity of the mode coupling equations, it is thus a pure dynamical transition and no thermodynamic phase transition is present.

The physical explanation about the microscopic origin of the slowing down is generally believed to be the cage effect, implemented by the kernel $m_q(t)$. A particle of the fluid does not perform a Brownian motion but rather rattles many times inside cages formed by its neighbors. The motion of a particle over distances larger than the typical cage size is severely suppressed when

the density is high, since the breaking of this cage requires a cooperative rearrangement of many particles; a slow complex dynamics is originated.

The essence of the mode coupling approximation is factorization of averages of products into products of averages. A priori estimations of the validity of the mode coupling approximation are not known. The approximation is uncontrollable in the sense that there is no systematic expansion scheme which would identify the considered expressions as some leading contributions in a series of terms of decreasing importance [41].

An interesting alternative derivation of MCT has been recently proposed [25]. This new approach is more transparent and allows to investigate in detail the meaning of the less controlled steps intrinsic in the original derivation of MCT. Starting from Newton's equations for the evolution of the density, one then writes them as a linear generalized Langevin equation, without the use of the projection formalism. A formally exact expression for the memory kernel is derived and, making the approximation that the noise is gaussian, the standard MCT equations are obtained, together with the random phase approximation for the static structure factor. This suggests that MCT is a theory of fluid dynamics that becomes exact in a mean field limit. This possibility will be confirmed in the next chapter on the basis of the strong analogies between the equations describing the schematic MCT and the dynamical equations of the p spin glass model with infinite range interactions. The basic steps of this new derivation of MCT are given in App. B.

2.1.1 Schematic models

Due to the complexity of the mode coupling equations, unfortunately their solutions can be obtained only numerically. Therefore Bentgzelius, Gotze and Sjolander made the approximation, which was proposed independently also by Leutheusser [20], that the structure factor is given by a delta function at a certain wave vector q_0 , which locates the main peak in S_q . With this approximation the system (2.3) reduces to a single equation for the only mode q_0 :

$$\ddot{\Phi}(t) + \Omega^2 \Phi(t) + \nu \dot{\Phi}(t) + \Omega^2 \int_0^t m(t-u) \dot{\Phi}(u) du = 0 \quad (2.6)$$

where $m(t) = F(V, \Phi(t))$ with $F(V, f) = \sum_n v_n f^n$. Such an equation for a single mode (or at most very few) is called a schematic model. Due to its greatly reduced complexity, analytic investigations are possible. Since in these simplified models the details of all the microscopic informations have been eliminated, they cannot be used to understand the experimental data quantitatively. However Gotze and Sjogren have found that many features of the general solutions near the singularity do not depend on the detailed form of the mode coupling kernel, but rather they are determined by a few parameters specifying the topological features of the singularity in the space of the parameters V ; therefore such universal features of the full theory can be discussed even with schematic models. Now we know how to construct schematic models in order to reproduce the desired features of the full MCT equations.

The simplest schematic model is the F_1 model with $F(V, f) = v_1 f$; it is analytically solvable and exhibits a A-type transition, i.e. the non-ergodicity parameter f vanishes regularly at the transition. More relevant to describe the structural glasses are those models with a B-type transition, where f discontinuously jumps to a nonzero value. Examples of this class are the F_{p-1} models, $F(V, f) = v_{p-1} f^{p-1}$, having for $p > 2$ the same qualitative features. In Chapter 3 we'll face a spin glass model, the p spin model, whose high temperature equilibrium dynamics is almost identical to the mode coupling theory described by the kernels F_{p-1} . Thus we'll discuss there this class of models in detail; they capture the most important features of the MCT, even if they display no stretched exponential usually found in the experimental studies of supercooled liquids. The simplest model, able to produce also stretching, is the $F_{1,2}$ model defined by $F(V, f) = v_1 f + v_2 f^2$. Its numerically obtained solution $\Phi(t)$ is showed in Fig. 2.1 for different values of the parameters.

2.2 Main results of MCT

MCT is characterized by many theoretical predictions [21, 22, 23, 24]. Most of them are obtained by asymptotic expansions near the glass singularity. In this section we present only some of the main predictions of MCT.

One of the main success of MCT is the prediction of the existence of the two

