SUPERCOOLED LIQUIDS, THE GLASS TRANSITION, AND COMPUTER SIMULATIONS

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1 Introduction

Although in everyday life glasses are mostly associated with pleasurable or useful things like a glass of wine or window pans, they have been, and still are, also the topic of research of an impressive number of investigations. In the last twenty years a particularly strong effort has been made to solve one of the long standing puzzles of condensed matter physics: The problem of the glass transition, i.e. to answer the simple question “What is a glass?” . The results of all these experimental, theoretical, and computational efforts is that today we have a much deeper understanding of the properties of glass forming systems. Nevertheless one must admit that despite the impressive activities in the field, some of the key questions are still not answered and therefore this subject is still a very active domain of research \[1,2,3,4\]. The goal of these lecture notes is therefore to serve as a simple introduction to the field, to familiarize the reader with some theories of the glass transition, and to discuss the results of some computer simulations that have been done to obtain a better understanding of glass-forming systems. Of course it will not be possible to present an exhaustive coverage of these different fields, since they are by now way to vast. But fortunately this is not really necessary because there exist quite a number of excellent textbooks and review articles that discuss the various aspects of glassy systems in more detail \[5, 6, 7, 8, 9, 10, 13, 12, 15, 14, 16, 17, 18, 19, 20, 21, 22, 23\]. Thus the goal of the present text is rather to provide a relatively concise introduction to these various fields and to allow the reader to familiarize him/her-self with this rapidly evolving topic.

In the first section we hence give an introduction to the dynamics of supercooled liquids and the glass transition. The second section is devoted to discuss some of the theoretical approaches used to describe these systems. Since computer simulations are one of the important current methods to study glass-forming materials, the following section will be devoted to discuss the advantages and disadvantages of simulations of such systems. Finally we will review some results of computer simulations of glass-forming liquids and discuss to what extend they can be used to check the validity of theoretical approaches and to increase our understanding of the static and dynamic properties of glassy materials.

2 Supercooled liquids and the glass transition: Important facts and concepts

The goal of this section is to give an introduction to some of the relevant properties of glass forming systems and to explain some of the pertinent concepts that are useful to characterize them. This overview is of course by no means exhaustive but it should nevertheless allow the reader to get familiar with these kind of systems. For a more exhaustive description we refer the reader to the additional literature mentioned in the text.

Let us consider a system in its liquid state. At sufficiently high temperatures it can be expected that the viscosity $\eta$ is small, the diffusion constant $D$ of the atoms (or more general of the constituent particles) is high, and that the typical relaxation time $\tau$ is microscopic, i.e. is on the order of a typical vibrational period of the system which for an atomic liquid is on the order of 0.1-1ps (see below for a precise definition of $\tau$). If the system is cooled below its melting temperature $T_m$ one can...
anticipate it to undergo a static phase transition, i.e. that it crystallizes. However, in practice it is found that most liquids can be supercooled to some extend, i.e. it is possible to study their properties in the (metastable) supercooled regime. (More details on the lifetime of this metastable state are given below.) Many experiments as well as computer simulations have shown that the structural as well as the thermodynamic properties of supercooled liquids show only a relatively weak temperature dependence and that this dependence can often be extrapolated smoothly from the data above \( T_m \). This is not the case for most dynamic properties, such as, e.g., quantities like the viscosity or the diffusion constant. Instead it is found that these properties usually show a \( T^{-\gamma} \) dependence that is much more pronounced than the one that would be expected from the one for the liquid above \( T_m \).

As a typical example for such a strong \( T^{-\gamma} \) dependence we show in Fig. 1 an Arrhenius plot of the viscosity \( \eta \). From this plot we recognize that a relatively modest change in temperature (depending on the material between 20% to a factor of 3) leads to an increase of \( \eta \) by about 12-14 decades. Note that the data shown covers a wide range of material, including oxides such as SiO\(_2\), as well as molecular liquids such as toluene. A similar behavior is also found for most polymeric systems. This shows that this dramatic slowing down of the dynamics is a very general phenomenon.

![Fig. 1. Temperature dependence of the viscosity of various glass-forming materials. Reproduced from Ref. [24] with permission.](image)

The materials shown in Fig. 1 have of course characteristic temperatures (melting point, etc.) that are very different and hence the different curves spread over a wide range of temperature. It is therefore useful to make a plot in which one tries to use a reduced temperature scale. One possibility to do this, proposed first by Laughlin and Uhlman, is to define a temperature \( T_g \) at which the viscosity of the system has the (somewhat arbitrary) value \( 10^{13} \) Poise (=10\(^{12}\)Pa s) and to plot the viscosity as a function of \( T_g/T \). An example of such a presentation of the data is shown in Fig. 2 and is commonly called “Angell-plot”. We see that in this type of plot the curves for the different materials seem to show a relatively simple pattern: There are liquids for which \( \eta(T) \) is to a very good approximation just an Arrhenius law (top curves in the diagram). A prototype of such a material is SiO\(_2\) who shows in the whole accessible temperature range this \( T^{-\gamma} \) dependence. If one moves downwards in the diagram, one finds materials whose viscosity shows a bending at intermediate values of \( T_g/T \). Finally the bottom curves show a quite pronounced curvature at a temperature around \( T_g/T \approx 0.7 \). Note that each curve can be parametrized in the form \( \eta(T) = \eta_0 \exp(E(t)/k_B T) \), by definition of \( E(t) \), and hence the local slope of the curves can be interpreted as a (temperature dependent) activation energy \( E(t) \). Hence one concludes from the figure that there are systems for which this activation energy is basically independent of temperature and others for which it increases rapidly with decreasing \( T \). This is evidence that for the first type of systems the mechanism related to the relaxation of the liquid is independent of temperature, whereas for the latter type it depends on \( T \). Hence Angell coined the terms “strong” and “fragile” to distinguish these two types of behaviors [25]. One possibility to characterize “fragility” in a quantitative way is to consider the slope of \( \log(\eta(T)) \) vs. \( T_g/T \) at \( T_g \): Large slopes correspond to fragile glass-formers and small ones to strong glass-formers. Although presently
it is not very clear what distinguishes strong and fragile glass-formers on a microscopic level, it has been found empirically that there is a significant correlation between fragility and other properties of the material ($T$ dependence of the specific heat, time dependence of relaxation dynamics, etc.) [26]. Furthermore one observes the trend that the structure of strong glass-formers is often given by a relatively open network (e.g. in the case of silica by corner-shared tetrahedra) whereas the structure of fragile systems is more often compact, such as a hard sphere system. Hence one can conclude that the fragility is a quantity that does have some physical significance and later on we will come back to this point.

Fig. 2. Viscosity of various glass-forming liquids as a function of $T_g/T$, where $T_g$ is the glass transition temperature defined via $\eta(T_g) = 10^{13}$ Poise. Reproduced from Ref. [24] with permission.

Starting from Fig. 2 it is now possible to formulate some of the pertinent questions in the field of glass-forming materials. The first one is clearly that one wants to understand what the reason is for the dramatic slowing down of the dynamics. As mentioned above, all the structural quantities investigated so far do not show any sign of a unusual $T$ dependence. This is in contrast, e.g., to the case of second order phase transitions where the slowing down of the dynamics upon approach to the critical point is closely related to the presence of a divergent length scale [27]. Thus for the present time it seems necessarily to look for another mechanism and in Sec. 3 we will discuss different theoretical approaches. Note that it is not even clear whether there is only one mechanism or whether there are several ones. E.g. it might well be that the slowing down at small and intermediate $\eta$ is governed by one mechanism and that at high $\eta$ a different mechanism becomes important. Such a crossover scenario might e.g. be used to rationalize the bending seen in the viscosity data for fragile systems.

A further important question, which is related to the first one, is the exact $T$ dependence of $\eta(T)$ and whether or not this dependence is the same for other typical time scales of the system, such as the diffusion constant or the relaxation time. It is found that at sufficiently high temperatures most liquids show an Arrhenius dependence. At intermediate and low temperatures the data can often, but not always!, be fitted well by the so-called Vogel-Fulcher(-Tammann)-law [28, 29, 30] which has the form

$$\eta(T) = \eta_0 \exp\left(\frac{A}{T - T_0}\right).$$  \hspace{1cm} (2.1)

Thus this functional form predicts a $T$ dependence that for temperatures close to $T_0$, a temperature...
that is usually called “Vogel-temperature”, is significantly stronger than a simple Arrhenius law. (Note that the latter corresponds to the special case $T_0 = 0$.) Although this type of fit gives a good representation of the data, there is no theoretical foundation for this Ansatz. Nevertheless it is very useful since it allows for a simple parametrization of the data with a quite good accuracy. (We point out, however, that there is experimental evidence that the Vogel-Fulcher-law does not hold exactly (31).)

For intermediate values of $\eta$, i.e. $10^{-1} \leq \eta \leq 10^2$, one often finds that the data is also very well compatible with a power-law of the form:

$$\eta(T) = \eta_0(T - T_c)^{-\gamma}.$$  \hspace{1cm} (2.2)

This $T$-dependence is one of the major predictions of the so-called mode-coupling theory of the glass transition (MCT) (13, 15) and in Sec. 3 we will discuss this theory in more detail. The value of the “critical temperature” $T_c$ is often found to be around 20-30% above $T_g$. Since Eq. (2.2) predicts a divergence of the viscosity at $T_c \geq T_g$ it is clear that this functional form cannot be correct for temperatures close to $T_g$. Below we will show however, that for temperatures that are around $T_c$, the theory is able to rationalize many dynamical properties of supercooled liquids.

If the Vogel-Fulcher-law given by Eq. (2.1) would indeed hold down to the Vogel temperature $T_0$ one would have a true divergence of the viscosity at a finite temperature. Whether or not such a divergence really exists is one further fundamental questions in the field of glass-forming liquids. If the answer is positive it means that below $T_0$ the system is in an ideal glass state, i.e. it is in the global minimum of the free energy, if one considers only amorphous states and neglects the crystal. Note that unfortunately no experiment will be able to give an answer to this question since in practice it is not possible to equilibrate a real system at a temperature close to $T_0$ as can be seen as follows: Every experiment last only a finite time $t_{\exp}$, and hence it will not be possible to study the equilibrium properties of the system below a temperature $T_{g_{\exp}}$ where $T_{g_{\exp}}$ is given implicitly by the relation $\tau(T_{g_{\exp}}) = t_{\exp}$. Since $\tau(T)$ will show at $T_0$ the same divergence as $\eta(T)$ we have $T_{g_{\exp}} > T_0$. Thus the above posed question can be answered only analytically or (at least in principle) by computer simulations (see Sec. 4).

So far we have discussed the temperature dependence of macroscopic quantities, like the viscosity. However, many experiments, such as dynamic light scattering, inelastic neutron scattering, dielectric measurements, etc.) give also direct access to the time dependence of microscopic correlation functions, such as the density-density correlator. Since very often the mentioned macroscopic quantities can be expressed as the time integral over such correlation functions, the latter certainly contain more
information as the former. (Examples are the viscosity that is related to the integral over the stress-stress correlation function or the diffusion constant that is related to the integral over the velocity correlation function of a tagged particle \(F(q, t)\). In Fig. 1 we show in a schematic way the time dependence of a typical time correlation function \(\Phi(t)\) (e.g. the intermediate scattering function \(F(q, t)\) discussed in more detail in sections 3 and 5). The two curves correspond to two temperatures: One at which the system is in its normal liquid state and one at which it relaxes only slowly. At the high temperature the relaxation is relatively simple: At very short times, i.e. at times much shorter than the typical microscopic times, the time dependence is quadratic in \(t\). This follows directly from the Taylor expansion of the equation of motion for the particles \(\Phi(t)\). Due to this \(t^2\) dependence this time window is often called “ballistic regime”. For somewhat larger times the \(t\)-dependence \(\Phi(t)\) is governed by the interactions between the particles and hence it is called the “microscopic regime”. (In the context of the mean squared displacement of a tagged particle, see Fig. 15, we will discuss this regime in more detail.) For even longer times, the \(t\)-dependence of \(\Phi(t)\) is approximated well by an exponential function, i.e. the system shows a Debye-relaxation.

At low temperatures \(\Phi(t)\) shows a more complex time dependence. At short times one finds again the ballistic regime that is followed by the microscopic regime. In contrast to the correlator at high temperature, \(\Phi(t)\) now shows at intermediate times a plateau. The time window in which the correlator is close to this plateau is called the “\(\beta\)−relaxation”. Only for times that are much longer (note the logarithmic time scale!) the correlation function decays to zero. The time window in which \(\Phi(t)\) decays below the plateau is usually called the “\(\alpha\)−relaxation”. Note that the early part of the \(\alpha\)−relaxation coincides with the late part of the \(\beta\)−relaxation. The physical meaning of the plateau is given by the so-called “cage effect”. At low temperatures each particle is surrounded by neighboring particles that form a temporary cage around it. At very short times the particles move ballistically and thus the correlation function shows a \(t^2\)−dependence. At somewhat longer times the particles start to interact with their neighbors and the correlation function enters the microscopic regime. For intermediate times the particles are trapped by their neighbors and hence the correlation function is almost constant. Only for much larger times the particles are able to leave their cage and hence the correlator starts to decay to zero. In the context of the mean squared displacement of a tagged particle we will return to this trapped motion and will discuss it in more detail (see Fig. 15). In contrast to the case at high \(T\), the final decay of the correlation function is not an exponential. Although the precise form is not known, it can usually be approximated well by the so-called Kohlrausch-Williams-Watts function (KWW) \(A \exp(-t/\tau)^\beta\), often also called “stretched exponential”, which has the form

\[
\Phi(t) = A \exp \left( -\left(\frac{t}{\tau}\right)^\beta \right)
\]

Here \(A\) is an amplitude, \(\tau\) can be used to define a relaxation time, and \(\beta \leq 1\) is the KWW-exponent. Note that \textit{a priori} all three parameters will depend on the observable as well as on the temperature considered. However, sometimes it is found that in a substantial temperature regime the three parameters are independent of \(T\). In such a case a plot of the correlator vs. \(t/\tau\) will give a \(T\)-independent master curve and therefore one says that the system obeys the “time-temperature-superposition principle”.

The reason why a time correlation function shows at low \(T\) a non-Debye behavior, i.e. that \(\beta < 1\), is still a matter of debate. There are two extreme scenarios \(\[\[\]:\]:

1. The first one is that due to the disorder each particle of the system has a slightly different neighborhood. Hence also the relaxation dynamics (in particular its relaxation time) will differ from particle to particle. Therefore in this scenario, called “heterogeneous”, the stretching is due to the sum of many different Debye-laws with different relaxation times. In the second scenario, called “homogeneous”, the relaxation dynamics of the different particles is not that much influenced by the \textit{different} surrounding disorder. Instead the (general) presence of the disorder gives rise to a non-Debye relaxation for each particle. Understanding which one of these two extreme cases are seen in a real supercooled liquid is presently still a matter of research. \(\[\[\]:\]:\] But what is already quite clear is that the truth is somewhere in between.

\[\text{\footnotesize{\textsuperscript{1}Here we assume that this is a liquid that can be described by Newton’s equations of motion. For dissipative systems, such as colloidal particles, some of the statements have to be slightly modified.}}\]
The last time regime we mention is related to the so-called boson peak \[40,41\]. In many, but not all, structural glasses it is found that there exist vibrational excitations that have a frequency that is about one decade smaller than the typical vibrations in the system. The precise nature of these excitations is still a matter of debate \[42,43,44,45,46,47,48,49,50,51,52,53,54,55,56\]. Although they are usually studied in the frequency domain, where they give rise to a peak, the so-called boson peak (see Fig. 4) they also give rise to a feature in the correlation functions in the time domain, in that the latter show a small dip after the microscopic regime. For typical glass forming systems, like e.g. silica, the location of the peak in the frequency domain is around 1THz, which thus corresponds to a time scale of 1ps.

The definition of the various time regimes we just gave have of course also their counterpart in the frequency domain, i.e. the realm of many experimental techniques (neutron-and light scattering, dielectric measurements). If one calculates the time-Fourier transform of a correlation function and multiplies its imaginary part with \(\omega/2k_B T\), one obtains a frequency dependent susceptibility \(\chi''(\omega)\) \[32,33\]. In Fig. 4 we show schematically how \(\chi''(\omega)\) depends on the frequency. We recognize that in general the microscopic regime gives rise to one (or several) peaks in \(\chi''\). The boson peak regime as well as the \(\alpha\)-relaxation show up as distinct peaks. (Note however, that depending on how pronounced the associated excitations are, the former is sometimes only a weak shoulder on the low-frequency side of the microscopic peaks.) Since in the time domain the \(\alpha\)-relaxation quickly moves to larger times if \(T\) is decreased, one finds that in the frequency regime the \(\alpha\)-peak moves rapidly to lower frequencies. In contrast to this the microscopic peaks as well as the boson peak show only a very weak dependence on temperature.

Having discussed the temperature dependence of structural and dynamical observables, where the former is weak and the latter is very strong, we now turn our attention to thermodynamic quantities. Experimentally it is found that most thermodynamic quantities, such as the pressure, specific heat, enthalpy, etc. show a very smooth and relatively mild \(T\)-dependence. (Note that we talking about the liquid like phase, i.e. we are not considering non-equilibrium effects that are seen at the glass transition. These will be discussed below in the context of Fig. 5.) In view of this it is surprising that in 1948 Kauzmann reported that the entropy of supercooled systems indicate the existence of a phase transition at sufficiently low temperature and in the following we will review the arguments that led to this conjecture. In Fig. 5 we show schematically the temperature dependence of the specific heat of a glass-forming system. Also included is the specific heat for the corresponding crystalline system. The latter curve exists only up to the melting temperature \(T_m\) and depends only weakly on \(T\), since anharmonic effects are usually small. The specific heat of the liquid like branch is higher than the one of the crystal since the liquids is able to flow, i.e. there are configurational degrees of freedom (those that give rise to the relaxation/flow of the system) than are not present in the crystal. Recall that at sufficiently low temperature the typical time correlation functions of a glass-forming liquid show a separation of time scales: At short times the particles vibrate in their cage and only at much longer times they are able to leave this cage and hence allow the system to flow (see Fig. 3). Hence also...
the specific heat can be split up into two contributions: One that is related to the vibrational degrees of freedom and a second part that is related to the relaxation dynamics (also called “configurational degrees of freedom”). (For a more formal approach to this splitting, see Refs. [57, 58].) The former is quite similar to the one in a crystal and shows also a similar temperature dependence. Hence the difference in $C$ between a supercooled liquid and the corresponding crystal is indeed given by the configurational degrees of freedom.

Using the $T$-dependence of the specific heat it is possible to calculate the entropy $S(T)$ in the liquid and crystalline phase by means of a thermal integration, i.e. by using the equality

$$S_\alpha(T_m) = S_\alpha(T) + \int_T^{T_m} dT \frac{C}{T} \quad \alpha \in \{\text{liquid, crystal}\}.$$  \hspace{1cm} (2.4)

With this relation it is thus possible to calculate $\Delta S$, the difference between the entropy of a liquid and the one of the crystal. The $T$-dependence of this difference, normalized by its value at the melting

Fig. 6. Schematic plot of the temperature dependence of the normalized difference between the entropy of the liquid state and the one of the crystalline state. The upper and lower curve correspond to the case of strong and fragile glass-forming material. Note that in the latter case a reasonable extrapolation of $\Delta S$ seems to vanish at a finite temperature, the so-called Kauzmann temperature.
temperature, looks schematically as drawn in Fig. 6. We see that for fragile systems this difference decreases rapidly with decreasing temperature and a reasonable extrapolation seems to indicate that it vanishes at a finite temperature $T_K$, the so-called Kauzmann temperature. Thus for $T < T_K$ the extrapolation predicts that the entropy of the glass is below the one of the crystal. Since in the liquid as well as in the crystal the total entropy is the sum of the entropy associated with the vibrational degrees of freedom and the entropy related to the configurational degrees of freedom, $\Delta S = 0$ implies that there configurational entropies of the glass and of the crystal are equal. This is of course a rather surprising result since the configurational entropy of the (ideal) crystal is zero, since there exists only one configuration and hence $\Delta S = 0$ implies that there exists also only one configuration for the glass. Hence for temperatures below $T_K$ the liquid cannot flow anymore, since there is not state to go to. Thus this final state can be considered as the “ideal glass”. However, Stillinger has put forward a simple argument that shows that in a system with short range interactions the existence of one glass state implies immediately that there are exponentially many (in the system size) and that therefore the configurational entropy of the disordered state remains always finite [59]. Thus one must conclude that sufficiently close to $T_K$ the extrapolation shown in Fig. 6 is no longer reliable and hence $\Delta S$ does not really vanish. (See also Ref. [60].)

It is remarkable that the apparent vanishing of $\Delta S$ at $T_K$ seems to be related also to the dynamics of the system in that it is found that often the value of the Vogel temperature $T_0$ from Eq. (2.1) is very close to $T_K$ [61]. One possibility for such a connection is given by the relation proposed by Adams and Gibbs [62], who used some phenomenological arguments to argue that

$$\tau(T) = A \exp \left( \frac{B}{k_B T S_{\text{conf}}} \right),$$

(2.5)

where $A$ and $B$ are constants and $S_{\text{conf}}$ is the configurational entropy. If one makes the Ansatz $S_{\text{conf}} \propto T - T_K$, Eq. (2.5) gives immediately the Vogel-Fulcher-law from Eq. (2.1) with $T_0 = T_K$.

![Fig. 7. Schematic plot of the temperature dependence of the volume (or enthalpy) of a glass-forming liquid that is cooled with a cooling rate $\gamma_i$ (thin lines) and reheated with the heating rate $\gamma'_i$ (dotted lines). The bold solid line is the curve for equilibrium.](image)

The results discussed so far concern the behavior of a glass-forming system in its equilibrium state (leaving out of course the possibility of crystallization). However, since the typical relaxation time of the system increases rapidly with decreasing $T$ it is not possible to equilibrate the system at arbitrarily
low temperatures since the glass transition intervenes. This is explained schematically in Fig. 7, where we show how the volume (or the enthalpy, or most other thermodynamic quantities) depend on temperature in a system that is subject to a quench. The bold solid curve shows the $T$–dependence of the volume in equilibrium. Let’s assume that we have equilibrated the system at a high temperature and want to cool it to a lower temperature. For this we have to couple it to a heat bath and cool the system with a cooling rate $\gamma_1$. Since the relaxation time increases with decreasing $T$ there will exist a temperature $T_{g1}$ below which the system is no longer able to equilibrate on the timescale $1/\gamma_1$ and hence it will fall out of equilibrium, i.e. it will undergo a glass transition (thin solid lines in Fig. 7). If we repeat the experiment with a cooling rate $\gamma_2$ the system will fall out of equilibrium at a temperature $T_{g2} < T_{g1}$ (see Fig. 7). Hence we see that the glass transition temperature is not a system intrinsic temperature (such as the melting temperature), since it depends on experimental parameters like the cooling rate etc. We emphasize that this dependency of $T_g$ is not just of theoretical interest but is indeed observed in real experiments or computer simulations [63, 64, 65, 66, 67, 68, 69, 70, 71]. In Sec. 4 we will come back to this point. In addition it must be expected that the system will already start to equilibrate, since the available time scale for a change in temperature is higher than the one the system had during the cooling ($\gamma_2 < \gamma_1$!). Hence the heating curve will bend downwards toward the equilibrium line. Thus we conclude that slightly below $T_{g1}$ the properties of the system will depend on time.

Since the glass transition temperature depends on the cooling rate, also the resulting glass will depend on $\gamma$ (see discussion in context of Figs. 1 and 13). Since the glass is an out of equilibrium state, all its properties depend on time, i.e. it is aging [72, 73, 74]. E.g. this can be seen if we start to heat a glass from low to high $T$. This is shown in Fig. 7(dotted lines). Let’s start with the glass that has been produced with a cooling rate $\gamma_1$. If we heat it with a heating rate $\gamma_2' = \gamma_2 < \gamma_1$ it will at low $T$ follow the cooling curve. However, for temperatures slightly below $T_{g1}$ the system will already start to equilibrate, since the available time scale for a change in temperature is higher than the one the system had during the cooling ($\gamma_2 < \gamma_1$!). Hence the heating curve will bend downwards toward the equilibrium line. Thus we conclude that slightly below $T_{g1}$ the properties of the system will depend on time.

If the initial glass is heated with the same rate as it has been cooled, the effect that we just mentioned is much less pronounced (see dotted curve for system $\gamma_2$). Hence the heating curve tracks very closely the cooling curve and only very closely to $T_{g2}$ one finds a small aging effect.

If the heating is faster than the cooling, see curve $\gamma_3$ in the figure where we assume that $\gamma_3 < \gamma_2$, the system does not show pronounced aging until $T_{g3}$. Due to the “high” heating rate it will, however, not be able to start to equilibrate even if it is at a temperature slightly above $T_{g3}$, since the relaxation times are still too large. Hence it will follow a smooth extrapolation of the “glass-like” branch of the volume. Only when the system has reached a temperature close to $T_{g2}$ the relaxation times will be short enough so that the system can equilibrate.

From this discussion it is clear that the falling out of equilibrium is an effect that depends crucially on the kinetics of the system and hence on the various time scales of the system and the experiments (cooling rate, the temperature dependence of the relaxation time and hence on the observable considered). For technical applications (manufacturing of glasses, improving the properties of glassy materials) it is important to have a good understanding of all these kinetic processes and therefore approximate schemes have been proposed already long time ago to describe them [73, 74, 75, 76, 77]. Although these approaches are useful to characterize the kinetics of the glass transition, they are of purely phenomenological nature and hence should not be confused with the much more recent and advanced theories of aging [79, 80, 74] despite the fact that often the same nomenclature is used (such as “fictive temperature of the glass”). For more details on these phenomenological theories we refer the reader to Refs. [51, 71].

Everything that we have discussed so far has been made under the hypothesis that the liquid does not crystallize even in its supercooled state. Although such an assumption is perfectly valid from a theoretical point of view, most real supercooled liquids do crystallize after some time (note that, however, there are liquids that do for all practical purposes indeed not crystallize, such as atactic polymers). In Fig. 8 we plot schematically $t_c$, the time needed for a liquid to crystallize as a function of its temperature. We see that if the supercooling is weak, the system can stay in this metastable state for a long time. Upon further supercooling the driving force for the nucleation and subsequent
crystallization increases and hence the crystallization time decreases rapidly (note the logarithmic time axis!). However, in order to form a critical nucleus it is necessary that the particles move and as we have discussed above this dynamics slows down quickly with decreasing $T$ (see dashed curve in the figure). Therefore at low $T$ the nucleation rate starts to decrease and hence the time for crystallization increases again. Hence we see that there is a temperature $T_{\text{max}}$ at which the crystallization rate has a maximum. Depending how large this maximal rate is, it may or may not be possible to study the system experimentally around $T_{\text{max}}$. Note, however, that depending on the details of the shape of the crystallization curve it might be possible to obtain an equilibrated liquid also below $T_{\text{max}}$, e.g. by quenching the system sufficiently quickly and thus passing this critical temperature. We emphasize that this schematic diagram can also be obtained for real glass-forming systems (see, e.g., Ref. [82]) and thus it is not just of theoretical value. One important consequence of the plot is that it shows that in principle any liquid/material can be used to form a glass. The only prerequisite is that one needs an experimental setup to do a sufficiently fast quench. Finally we remark that since the curves relate temperature, time and transformation to the crystalline phase, this plot is usually called “$T\ T\ T$—diagram”.

The slowing down of the relaxation dynamics that we have reviewed so far was due to a change in temperature. It is important to realize, however, that this is by no means the only possibility to slow down the dynamics of a system. Other possibilities include an increase of pressure, evaporation of a solvent in a polymeric system, increasing the density of crosslinks in polymers, etc. Although these routes to slow down the system have so far been investigated less than the temperature route, they are perfectly valid protocols to study the relaxation dynamics of glass forming systems. As we have mentioned above, the glass transition is just a kinetic phenomenon in which the time scale of the experiment becomes comparable with the relaxation time of the system. It is, however, possible to produce glasses also without ever going to high temperatures. E.g. one can irradiate a crystal with neutrons and the so induced radiation damage will slowly transform the sample into a glass [83]. The same is true if one compresses a crystal beyond its stability limits or if one grinds a crystalline material. Another possibility to form a glass is to deposit vapor onto a old surface or to make a chemical reaction (sol-gel transition) [84, 85]. It has to be emphasized that glasses produced in these different ways will in general differ in their properties even if some of their macroscopic properties (density, etc.) are the same. Strictly speaking it is therefore necessary not only to list some of the properties of a given glass to characterize the material, but also to specify its complete history of production.

Most of the systems we discussed in this section were liquids in their supercooled state. We emphasize, however, that a slow relaxation dynamics is not necessarily related to the supercooled
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state. E.g. for the case of SiO$_2$ the glass transition temperature is $T_g = 1450$K and the melting temperature is 2000K. From Fig. 2 one recognizes that at $T_g/T_m = 0.725$ the viscosity has already a value of $10^7$Poise, i.e. the system is already very viscous (recall that water at room temperature has a viscosity around $10^{-2}$Poise!). Therefore we conclude that in order to understand the reason for the slow relaxation of a system, its supercooled state cannot be a relevant factor. For this reason one sometimes also uses the term “glassy liquids” if one wants to describe a liquid whose relaxation time is already much larger than the typical microscopic time scale. In the following we will, however, use the terms “supercooled liquids” and “glassy liquids” interchangeably.

Before we end this section we briefly summarize some of the salient features of glass-forming systems:

- presence of disorder and/or frustration (in the structure, in the interactions, . . . )
- no obvious presence of long range order
- strong dependence of the relaxation time on an external parameter (temperature, pressure, . . . )
- transition to a non-erotic phase
- non-exponential decay of the relaxation function at low temperatures

Of course this list is neither complete nor is it necessary that every glass-forming system has all these properties. Instead this list should give an idea what one typically finds in glass-forming systems and therefore help to answer the question asked in the Introduction: “What is a glass”. Using this “definition” one realizes that the class of glass-forming systems is very large: Apart from the atomic and molecular liquids that we have considered so far, there are the huge class of polymeric systems that are of immense importance in our daily life. Of equal relevance are granular materials (sand, flour, . . . ) who share many properties of structural glasses at low temperatures. Foams and spin glasses are other systems that share many properties with glass-forming liquids. Last not least many optimization problems (folding of proteins, traveling salesman problem, “k-sat problem”) have a landscape of the cost function that is very similar to the one of the potential or free energy of more standard glassy systems and therefore some of the ideas and concepts used in the later systems are useful in the former as well.

The Mode-Coupling Theory of the Glass Transition

The subject of this section is the above mentioned mode-coupling theory of the glass transition. Unfortunately the derivation of all the needed equations is well beyond the scope of this article and therefore we will refer the reader to the more specialized literature (see also the review articles in Refs. [13, 15, 88, 89, 90, 91]). Nevertheless, the predictions that MCT makes are quite simple to understand and therefore we will discuss them in the following. In addition the theory has the remarkable advantage that it makes detailed qualitative or even quantitative predictions that can be tested in experiments or in computer simulations, which is in contrast to most other theoretical approaches in this field.

The starting point of MCT is the hypothesis that all the structural properties of a glass-forming liquid are very similar to the one of the “normal”, i.e. high temperature, liquid. As we have seen in the previous section this assumption is well founded. The second important step in the theory is to exploit the fact that supercooled liquids show a separation of time scale, i.e. that there are dynamical processes, such as vibrations, that occur on a microscopic time scale and others, such as the relaxation, that are observed on a time scale that can be many orders of magnitude longer than the former one. MCT makes use of this property of glassy liquids by i) making the choice that the relevant slowly varying observables are given by the density distribution of the particles and ii) by deriving equations of motion for these slow variables. To obtain these equations of motion, the theory makes use of an exact formalism that is called the Zwanzig-Mori projection operator formalism [12, 93]. Since this formalism is very useful to understand the structure of the final MCT equations we will now discuss this approach in somewhat more detail.
3.1 The Mori-Zwanzig formalism

We start with a general classical $N$-particle system. The equation of motion for an arbitrary phase space function $g$ is given by

$$\dot{g} = iLg = \{H, g\}, \quad (3.1)$$

where $L$ and $H$ are the Liouville operator and the Hamiltonian, respectively, and $\{,\}$ are the Poisson brackets. It is clear that the set of all possible phase space functions form a vector space and that one can define a scalar product $(g|h)$ on this space via

$$\langle g, h \rangle = \langle \delta g^* \delta h \rangle, \quad (3.2)$$

where $\langle . \rangle$ is the usual canonical average, and $\delta g = g - \langle g \rangle$, i.e. is the fluctuating part of $g$.

Let us assume that thanks to some physical insight we have understood that the phases space variables $A_n$, $n = 1, \ldots k$ vary only slowly with time. In the following we will derive equations of motion for these variables that we will denote by $A$. In a first step we define an operator $P$ that projects an arbitrary function $g$ on the space spanned by the subset $A_n$:

$$P(g) = (A, g)(A, A)^{-1}A = \sum_{n,m} [A_n][(A_i, A_j)]^{-1}_{nm} (A_m|f) \quad (3.3)$$

where $[(A_i, A_j)]^{-1}_{nm}$ is the $n, m$ element of the inverse of the matrix $(A_i, A_j)$. Furthermore we define the projection operator $Q = 1 - P$. It is easily verified that $P$ and $Q$ are indeed projectors, i.e. that e.g. $P^2 = P$.

From Eq. (3.1) it follows that the time dependence of $A$ is given by $A(t) = \exp(iLt)A$. Inserting the identity operator $P + (1 - P)$ after the propagator $\exp(iLt)$ and differentiating this equation with respect to $t$ one finds

$$\frac{dA}{dt} = \exp(iLt)[P + (1 - P)]iLA = i\Omega \cdot A(t) + \exp(iLt)(1 - P)iLA \quad (3.4)$$

where we have introduced the so-called frequency matrix $i\Omega = (A, iLA) \cdot (A, A)^{-1}$. The last term in Eq. (3.5) can be written as

$$\exp(iLt)(1 - P)iLA = \int_0^t d\tau \exp[iLa(t - \tau)]iP Lf(\tau) + f(t) \quad (3.6)$$

where the function $f(t)$ is called “fluctuating force” (see below why) and is given by

$$f(t) = \exp[i(1 - P)Lt]i(1 - P)Lf(\tau) \quad (3.7)$$

Note that Eq. (3.7) shows that the time evolution of the function $f$ from its initial value $i(1 - P)Lf(\tau)$ is ruled by the propagator $\exp[i(1 - P)Lt]$ instead of the usual one: $\exp[iLt]$. In addition we also see immediately that due to the factor $(1 - P)$ we have

$$(A, f(t)) = 0 \quad (3.8)$$

i.e. $f(t)$ is always orthogonal to $A$.

Using in Eq. (3.4) the relations $PLf(\tau) = (A, Lf(\tau)) \cdot (A, A)^{-1}A$ and $i(A, Lf(\tau)) = i((1 - P)Lf(\tau), f(\tau))$, we obtain for the equation of motion (3.3) the expression

$$\dot{A} = i\Omega \cdot A(t) - \int_0^t d\tau M(\tau) \cdot A(t - \tau) + f(t) \quad (3.9)$$
where we have introduced the memory function $M(t) = \langle f \cdot f(t) \rangle \cdot (A, A)^{-1}$. The equation of motion for $C(t) = \langle A^\ast(0) A(t) \rangle$, the matrix of the correlation functions, is now easily obtained by multiplying Eq. (3.9) with $A$:

$$\dot{C}(t) = i\Omega \cdot C(t) - \int_0^t d\tau M(\tau) \cdot C(t - \tau) \ .$$

(3.10)

Note that the third term on the right hand side of Eq. (3.9) does not show up in Eq. (3.10) due to Eq. (3.8). Equations (3.9) and (3.10) are usually called generalized Langevin equation and memory equation, respectively. Both of them are exact since no approximation has been made so far. The formal solution of Eq. (3.10) is obtained by introducing the Laplace transformed quantities

$$\tilde{C}(z) = \int_0^\infty dt \exp(-zt)C(t) \quad \text{and} \quad \tilde{M}(z) = \int_0^\infty dt \exp(-zt)M(t) \quad (3.11)$$

which give

$$\tilde{C}(z) = \left[zI - i\Omega + \tilde{M}(z)\right]^{-1} \cdot \tilde{C}(0) \ .$$

(3.12)

Here $I$ is the unit matrix. Although this solution is formally exact, it is not that useful since the time dependence of the memory function $M(t)$ is very complicated. However, if the set $A$ of variables that we have chosen includes all slowly varying quantities, the memory function must either be a fast variable, or it must be possible to express it (at least approximately) as a function of the variables in $A$, such as, e.g. as linear combinations of $A_i^n A_j^m$, with $n, m = 1, 2, \ldots$. This coupling of the variables (modes) has given rise to the name “mode-coupling theory”. We emphasize that the Mori-Zwanzig projection operator formalism and the mode-coupling approximations are not just a technique to describe the dynamics of supercooled liquids but a method that has been widely used in all sort of situations where one is able to identify pertinent slow variables (critical phenomena, Brownian motion, etc.) [94, 95]. Whether or not this approach is successful depends of course on the situation of interest and it is in most cases difficult to tell in advance. However, it has been found that there are indeed quite a few situations in which this method works remarkably well.

### 3.2 Application of the Mori-Zwanzig formalism to glass-forming systems

Having discussed the general formalism that leads to mode-coupling equations, we now turn our attention back to the case of supercooled liquids. For this type of systems it has been proposed that the slow variables are $\delta\rho(q, t)$, the fluctuations in the density for wave-vector $q$, and hence the mode-coupling equations are equations of motion for the corresponding correlation functions $F(q, t)$:

$$\delta\rho(q, t) = \sum_{j=1}^N \exp[iq \cdot r_j(t)] \quad \text{and} \quad F(q, t) = \frac{1}{N} \langle \delta\rho(q, t) \delta\rho(q, 0)^\ast \rangle \quad (3.13)$$

(Note that here we have assumed that the system is isotropic. Hence $F(q, t)$ depends only on the modulus of $q$. Also important is the fluctuation in the density of a tagged particle $\delta\rho_s(q, t)$ for wave-vector $q$ and its associated correlation function $F_s(q, t)$:

$$\delta\rho_s(q, t) = \exp[-iq \cdot r_j(t)] \quad \text{and} \quad F_s(q, t) = \frac{1}{N} \langle \delta\rho_s(q, t) \delta\rho_s(q, 0)^\ast \rangle \quad (3.14)$$

(Note that due to the thermal average in the definition of $F_s(q, t)$, the correlator does not depend on the particle index $j$.) The space-time correlation functions $F(q, t)$ and $F_s(q, t)$ are usually called the coherent and incoherent intermediate scattering functions [22]. Apart from their theoretical importance, their significance lies in the fact that they are directly accessible in inelastic neutron scattering [23, 24]. Hence obtaining a good understanding of their $q$ and $t$–dependence is considered a very important task in the theory of liquids (which is not yet a solved problem).
A somewhat lengthy calculation shows that the MCT equations for $\Phi(q,t) = F(q,t)/S(q)$, where $S(q) = F(q,0)$ is the static structure factor, are given by \[97, 13, 143, 98, 99]:

$$
\dot{\Phi}(q,t) + \Omega^2(q)\Phi(q,t) + \int_0^t \left[ M^{\text{reg}}(q, t - t') + \Omega^2(q)M(q, t - t') \right] \Phi(q, t') dt' = 0.
$$

(3.15)

Thus we see that this equation does indeed have the form of the general mode-coupling equation (3.11). The value of the squared frequency $\Omega^2(q)$ follows directly from the short time expansion of the equations of motion for the particles and is given by

$$
\Omega^2(q) = q^2 k_B T/(mS(q)),
$$

(3.16)

where $m$ is the mass of the particles. The function $M^{\text{reg}}(q, t)$, also often called the “regular part of the memory function, governs the time dependence of $F(q,t)$ at short (i.e. microscopic) times, e.g. just after the ballistic regime. Often it is modeled by a Gaussian Ansatz \[98, 99\], but its precise functional form is presently not really known. Note that this part of the memory function is present also in “normal” liquids (i.e. liquids that are not glassy) where it governs the relaxation dynamics and thus obtaining an accurate form of the $M^{\text{reg}}(q,t)$ is a current problem of standard liquid state theory.

The long time behavior of $\Phi(q,t)$ is ruled by the memory function $M(q,t)$. Within the approximation of MCT this kernel is a quadratic function in $\Phi(q,t)$:

$$
M(q,t) = \frac{1}{2(2\pi)^3} \int d^3k V^{(2)}(q, k, |q - k|)\Phi(k, t)\Phi(|q - k|, t)
$$

(3.17)

where the vertex $V^{(2)}$ is given by

$$
V^{(2)}(q, k, |q - k|) = \frac{n}{q^2} S(q)S(k)S(|q - k|) \left( \frac{q}{q |k c(k) + (q - k)c(|q - k|)|} \right)^2.
$$

(3.18)

Here $n = V/N$ is the particles density and $c(k)$ is the so-called direct correlation function that is related to the structure factor via $c(k) = n(1 - 1/S(q))$ \[32\]. Hence we see that Eq. (3.17)-(3.18) are a closed set of equations that define the time dependence of $\Phi(q,t)$ and hence of $F(q,t)$. Thus the solution of this set of equations are correlation functions that can in principle be directly compared with data from an experiment or a computer simulation.

Some remarks on these equations and their solutions:

- The form of Eq. (3.15) is the one of a damped harmonic oscillator with a damping that depends on time. With decreasing temperature the static structure factor becomes more peaked and hence also the vertices $V^{(2)}$ become more peaked. This means that the damping $M(q,t)$ increases, at least for certain wave-vectors, and that hence the relaxation becomes slower. Note that since the memory function depends itself on the correlators, see Eq. (3.15), a slowing down of the latter will increase the former, therefore leading to an even slower dynamics for $\Phi(q,t)$. This non-linear feedback effect leads to a very strong dependence of the relaxation dynamics on the structural quantities and hence gives a qualitative explanation why the relaxation times of glass-forming systems change so quickly as a function of external parameters (temperature, pressure, etc.).

- It can be shown that if the vertices are sufficiently large, the time scale at which the correlators start to decay to zero increases beyond any bound. This means that there is a critical temperature $T_c$ (or pressure $p_c$) at which the correlators do not decay to zero anymore and hence at which the system undergoes a transition from an ergodic state to a non-ergodic one. Often this is called an “ideal glass transition” or the “mode-coupling transition”. Due to this ideal transition the equations are also called “ideal mode-coupling equations” and at the end of this section we will briefly discuss their generalization.
The only input needed to solve these equations are the static quantities \( S(q) \), \( m \), \( n \) and \( T \). In addition there is the memory function \( M^{\text{reg}}(q,t) \) for the dynamics at short times. However, it can be shown that the details of \( M^{\text{reg}}(q,t) \) do neither affect the existence of the MCT-transition nor the value \( T_c \) at which it occurs. Also the \( t \)-dependence of \( F(q,t) \) at intermediate and long times, i.e. times much longer than the microscopic times, is independent of \( M^{\text{reg}}(q,t) \), apart from a system universal shift in the time scale. Hence MCT predicts that the relaxation dynamics is completely independent of the microscopic dynamics, apart from a overall change of the time scale.

The equations of motion discussed so far concerned only the auto-correlation function for the coherent intermediate scattering function \( F(q,t) \). However, it is possible to derive also equations of motion for the incoherent function \( F_s(q,t) \), defined in Eq. (3.14). One finds that these equations have the following form:

\[
\ddot{F}_s(q,t) + \frac{q^2 k_B T}{m} F_s(q,t) + \int_0^t \left[ M^{\text{reg},s}(q,t-t') + M^s(q,t-t') \right] \dot{F}_s(q,t')dt' = 0 \tag{3.19}
\]

Here the memory function is given by

\[
M^s(q,t) = \frac{n k_B T}{(2\pi)^3 m} \int dq' \left( \frac{k' \cdot q}{q} \right)^2 c(q') S(q') \Phi(q',t) F_s(|q-q'|,t) \tag{3.20}
\]

Thus the memory function for the dynamics of \( F_s(q,t) \) contains the normalized coherent intermediate scattering function \( \Phi(q,t) \) and hence we see that in order to obtain the time dependence of \( F_s(q,t) \), we need first the one for \( F(q,t) \). This result is quite reasonable, since \( F_s(q,t) \) describes the motion of a tagged particle in its environment (which is disordered and time dependent). Hence it must be expected that a relevant input for the time dependence of \( F_s(q,t) \) is the time dependence of the relative motion of the tagged particle with respect to its surrounding, and \( F(q,t) \) provides exactly this kind of information.

The vertices \( V^{(2)} \) as given by Eq. (3.18) depend only on the static structure factor \( S(q) \). Strictly speaking this is not quite true, since there is also an additional term that depends on the three-particle correlation function known as \( c_3(q,k) \). However, for simple liquids it has been found that this additional contribution to \( V^{(2)} \) influences the quantitative predictions of the theory only very weakly and hence it is in most cases neglected. For the case of liquids that have a structure that is given by an open network, this is no longer true and hence these additional terms have to be taken into account. In context with Figs. 2 and 28 we will come back to this point.

So far we have only discussed one-component atomic liquids. It is relatively straightforward to generalize the MCT equations also to multicomponent systems and one finds that in that case the equations of motion become matrix-equations for the partial intermediate scattering functions.

It is also possible to take into account the situation that two (or more) particles are permanently linked together, which opens the door to obtain a description for the translational and orientational correlation functions in molecular and polymeric systems. The equations one obtains are, however, rather complicated and therefore difficult to solve numerically. However, if one is interested only in simple orientational correlation functions, it is possible to simplify these equations considerably and hence to treat such molecular systems also numerically.
task and therefore it would be nice to have some means to simplify these equations. One possibility for doing this has been proposed in a seminal paper by Bengtzelius et al. [13] (see also Leutheusser [15]). By solving numerically the MCT-equations for the case of a hard sphere system, these authors found that the main contribution to the memory function \( M(q,t) \) comes from wave-vectors that are close to the peak in the static structure factor. Hence they proposed to approximate the \( S(q) \) by a single \( \delta \)-function located at this peak: \( S(q) = \zeta \delta(q - q_0) \). Here \( \zeta \) is the strength of the \( \delta \)-function and thus is assumed to increase with decreasing temperature. It is now found immediately that the MCT-equations simplify significantly in that they boil down to a single equation of the form:

\[
\dot{\phi}(t) + \Omega^2 \phi(t) + \zeta \Omega^2 \int_0^t \phi^2(t - t') \dot{\phi}(t') dt' = 0 , \tag{3.21}
\]

where \( \phi(t) = F(q_0,t)/S(q_0) \) and we have neglected the regular part of the memory function \( M^{reg} \), since, as discussed above, it does not influence the solution of the equations qualitatively. If one approximates the structure factor by the sum of two \( \delta \)-functions, one obtains two equations of motion in which the memory function is a simple polynomial of the two correlators. The equations of motion obtained in this way are called “schematic models” and Eq. (3.21) is a particular example. The interest in such models lies in the fact that the generic features of their solutions are the same as the ones of the full MCT-equations. However, since they are significantly more simple that these full equations, they are very useful to obtain a general overview on the possible \( t \)-dependence of the solutions. In addition they have also been found to be very useful to discuss experimental data such as spectra of dynamical light scattering [110, 117, 113, 114].

Before we start to discuss the generic properties of the solutions of the MCT-equations we briefly mention a very interesting connection of these equations with the time-correlation functions of spin glasses [8, 20]. From the way the MCT-equations are derived it is clear that for the case of a real liquid they are only an approximation. Since this approximation is non-perturbative (there is no small parameter), the resulting equations have often been criticized as being “uncontrolled”. Although strictly speaking this might be true for the case of real liquids, it has been found that the predictions of the theory are often so remarkably good, see Refs. [13, 34, 21] for reviews and some examples will be discussed below, that the observed agreement cannot be a mere accident. Nevertheless it would of course be uncomfortable if one would know systems for which the MCT-equations are exact. Surprisingly such systems do exist, as has been shown in a series of seminal papers by Kirkpatrick, Thirumalai and Wolynes [120, 122, 123]. These authors found that in certain type of mean-field spin glasses (Potts glasses and \( p \)-spin models) the equation of motion for the spin-auto-correlation function obeys exactly the MCT-equations as given by the schematic models. Thus this surprising connection between the structural glasses and spin glasses gave evidence that these two type of systems, which at a first glance have very little in common, might be much more similar than has been anticipated. In recent years a large effort has been made to test to what extend this connection holds, i.e., to test whether concepts and ideas that work well for one type of system (overlap of states [23], violation of the fluctuation dissipation theorem in the glassy phase [8, 23], driving of the system, calculation of the Kauzmann temperature [24, 25, 26, 127], etc.) are also useful for the other type of disordered system. All these activities resulted that the field is currently still extremely active and highly interesting.

We now turn our attention to the discussion of some of the pertinent predictions of MCT. One of the most important prediction is the one already mentioned above, namely that there exists a critical temperature \( T_c \) at which the \( \alpha \)-relaxation time of the system diverges. All the other predictions that will be presented in the following hold, strictly speaking, only very close to \( T_c \), i.e. it is assumed that the parameter \( \sigma = (T_c - T)/T_c \) is small. How small in practice \( \sigma \) has to be so that the predictions of the theory hold is presently not very clear and depends also on which prediction one considers [122, 123]. The results of experiments and computer simulations have shown, however, that often it is sufficient that \( |\sigma| \) is less than 0.1-0.2, i.e the predictions of the theory can be seen in a reasonable interval of \( T \).

MCT predicts not only that the \( \alpha \)-relaxation time diverges at \( T_c \), but also gives the specific form of this divergence, namely a power-law:

\[
\tau_x(T) = C_x(T - T_c)^{-\gamma} . \tag{3.22}
\]
Here \( \tau_x(T) \) denotes the \( \alpha \)-relaxation time of a correlator that we label with \( x \) (e.g. this might be the relaxation time for the coherent intermediate scattering function for wave-vector \( q \), the incoherent function, etc.). \( C_x \) is a prefactor that depends on \( x \) and whose \( T \)-dependence close to \( T_c \) can be neglected, and \( \gamma \) is a system universal constant, i.e. it is independent of \( x \). Hence the implication of Eq. (3.22) is that all correlation functions will show a divergence of the relaxation time at the same temperature \( T_c \) and also the critical exponent \( \gamma \) will be independent of the correlator considered. (Note that by “all correlators” we mean here that the overlap of the observable of interest with \( \delta \rho(q,t) \) does not vanish.) One consequence of this result is that also the inverse of the diffusion constant \( D \) should show a power-law divergence, since \( D \) can be expressed as the limit \( q \to 0 \) of the incoherent intermediate scattering function. Hence we have:

\[
D^{-1}(T) \propto \tau_x(T) = C_x(T - T_c)^{-\gamma} .
\] (3.23)

If the MCT equations are solved numerically, it is found that with increasing coupling (i.e. decreasing temperature in Eqs. (3.17)-(3.18), or increasing \( \zeta \) in Eq. (3.21)) the time-dependence of the solution changes from a shape as given qualitatively by the high \( T \) curve shown in Fig. 2 to a shape as the one of the low \( T \) curve in this figure. Thus we see that the theory is able to describe the cage effect discussed in the previous section at least qualitatively. The theory goes, however, much further in that it does not only give a qualitative description of the cage effect but predicts that in the \( \beta \)-relaxation regime the time dependence of all correlation functions (“all” in the sense described above) is universal in the following sense: Let \( \Phi_x(t) \) be an arbitrary correlator. Then it is predicted that close to the plateau \( \Phi_x(t) \) can be written as

\[
\Phi_x(t) = \Phi_x^c + h_x G(t) ,
\] (3.24)

where \( \Phi_x^c \) is the height of the plateau (often also called “non-ergodicity parameter”, since it gives the fraction of the memory of the initial state that still exists in the time window of the plateau), \( h_x \) is an amplitude, and \( G(t) \) is a system universal function. Thus we see that the theory predicts that \( \Phi_x(t) - \Phi_x^c \) is just the product of a \( x \)-dependent amplitude and a \( x \)-independent function of time. Therefore the relation given by Eq. (3.24) is called the “factorization property”. Furthermore the theory predicts that the function \( G(t) \) has a very specific dependence on temperature in that it can be written in the form

\[
G(t) = \sqrt{\sigma} g_{\pm}(t/t_\sigma), \quad \sigma = (T_c - T)/T_c ,
\] (3.25)

where the \( T \)-independent functions \( g_{\pm} \) correspond to \( T < T_c \) and \( T > T_c \), respectively. The time scale \( t_\sigma \) is the location of the plateau and is predicted to show a power-law divergence of the form \( t_\sigma = t_0 |\sigma|^{1/2\alpha} \), where \( t_0 \) is a microscopic time scale.

The time dependence of the functions \( g_{\pm} \) can be obtained by solving (numerically) the following non-linear equations [30]:

\[
\mp z^{-1} + z g_{\pm}^2(z) + i \lambda \int_0^\infty d\tau \exp(i z \tau) g_{\pm}^2(\tau) = 0 .
\] (3.26)

Here the constant \( \lambda \), which is also often called “exponent parameter”, can be calculated from the vertices \( V^{(2)} \). Since the functions \( g_{\pm}(t) \) give the time dependence of the correlation functions in the \( \beta \)-relaxation regime, they are called “\( \beta \)-correlator”.

The solution of Eq. (3.26) are not known analytically but it can be shown that they have the following asymptotic form (i.e. very close to the plateau):

\[
g_{\pm}(\hat{t}) = \hat{t}^{-\alpha} \quad \text{for} \quad \hat{t} \ll 1, \quad \text{i.e.} \quad t_0 \ll t \ll t_\sigma
\] (3.27)

This functional form is called “critical decay”. For times much larger than \( t_\sigma \) the form of \( g_{-}(t) \) is given by

\[
g_{-}(\hat{t}) = B \hat{t}^b \quad \text{for} \quad \hat{t} \gg 1 \quad \text{i.e.} \quad t_\sigma \ll t \ll \tau ,
\] (3.28)
a functional form that in this context is called “von Schweidler law” \[130\]. The exponents \(a\) and \(b\) from Eqs. (3.27) and (3.28) can be calculated from the exponent parameter \(\lambda\) from Eq. (3.26) via

\[
\frac{\Gamma(1 - a)^2}{\Gamma(1 - 2a)} = \frac{\Gamma(1 + b)^2}{\Gamma(1 + 2b)} = \lambda,
\]

where \(\Gamma(x)\) is the usual \(\Gamma\)–function. Furthermore the theory makes the interesting prediction that the exponent \(\gamma\) of the power-law for the \(\alpha\)–relaxation time \(\tau\), see Eq. (3.22), is related to \(a\) and \(b\) by means of the relation

\[
\gamma = \frac{1}{2a} + \frac{1}{2b}.
\]

Hence we see that once the exponent parameter \(\lambda\) is known, the exponents \(a\), \(b\) and \(\gamma\) are determined.

Note that according to MCT the \(\beta\)–relaxation is not just the cross-over regime from the microscopic dynamics to the relaxation dynamics at long times, but it is a process of its own (that is, however, tightly connected with the \(\alpha\)–process). To understand what we mean by this we consider the imaginary part of a dynamical susceptibility which was shown schematically in Fig. 4. In the context of that figure we have said that with decreasing temperature the \(\alpha\)–relaxation peak moves quickly to the left, whereas the microscopic peak shows only a very weak \(T\)–dependence. Thus the existence of a minimum between the two peaks is of course trivial. The non-trivial statement of MCT is that close to the minimum \(\chi''(\omega)\) is not just the sum of the low-frequency part of the microscopic peak and the high-frequency part of the \(\alpha\)–peak, but that there is an additional intensity, the \(\beta\)–process that is described by the \(\beta\)–correlator occurring in Eq. (3.24).

Having discussed some of the predictions of MCT for the \(\beta\)–relaxation, we now turn our attention to the \(\alpha\)–relaxation, i.e. the time window in which the correlators fall below the plateau. In the context of Eq. (3.22) have already discussed one important property of this relaxation regime, namely that the relaxation times diverge at the same critical temperature and that also the exponent is the same. A further prediction of the theory is that the time-temperature superposition principles (TTSP), mentioned in Sec. 2, should hold. This means that at a temperature \(T\) the time dependence of a correlator \(\Phi(t, T)\) can be written as follows:

\[
\Phi(t, T) = \hat{\Phi}(t/\tau(T))
\]

where \(\hat{\Phi}\) is a master function, and \(\tau(T)\) is the usual \(\alpha\)–relaxation time. (Note that if the TTSP holds, the precise definition of \(\tau(T)\) is irrelevant for Eq. (3.31) to hold.)

As mentioned in Sec. 2, the shape of the correlators is usually approximated well by the KWW function given in Eq. (2.3). Although this function is not an exact solution of the MCT equations, it has been found that also the numerical solutions of the MCT equations are approximated very well by a KWW function. Hence it can be concluded that MCT is predicting the stretching of the time correlation function.

Before we end this section on MCT it is appropriate to make some comments to what extent this theory is applicable to real glass-forming systems. As mentioned above, the MCT equations are exact for certain mean-field models (see articles by Parisi and Cugliandolo in these proceedings \[123, 74\]). For short range systems the equations will of course only be an approximation and the real question is how good this approximation really is. Unfortunately there is presently no clear answer. There are short range spin glasses, e.g. the 10 state Potts model, whose static and dynamic properties are very different from the mean-field prediction, whereas in other spin glasses the mean-field prediction seems to be very reliable \[131, 132\]. For the case of structural glasses there is a large body of literature in which the applicability of MCT has been investigated for all sort of systems (colloids, gels, molecular glasses, network-forming glasses, polymers, etc.) and it has been found that in general the theory does a remarkably good job in explaining many dynamical features of these systems on a qualitative level, or sometimes even quantitatively (see Ref. \[11\] for a recent review of the experimental literature).

There are, however, also results from experiments or simulations that seem to be at odds with the predictions of the theory. A careful inspection of such findings shows that either the theory has
not been used in an appropriate way (e.g. because the authors have not fully understood the theory) or that only the asymptotic predictions of the theory have been tested. By “asymptotic predictions” we mean the following: As mentioned above, most predictions of the theory, and in particular the ones presented in this article, hold only very close to the critical point $T_c$. These predictions are nothing else than the mathematical properties of the solutions of the MCT equations, i.e. they are independent of whether whether or not these equations correctly describe a real system. If the parameter $\sigma = (T - T_c)/T_c$ cannot be considered as small anymore, these properties no longer hold and therefore the properties of the solutions change, and in particular they cannot be cast into simple forms as given, e.g., by Eqs. (3.27) or (3.28). Although even in such a case it is possible to make some analytical predictions that can be tested, it is in most cases simpler to make a direct comparison with the numerical solution of the MCT equations. However, this approach is quite involved and therefore not often done. But in principle it is the only systematic procedure if one really wants to find out whether or not the MCT equations give a good description of the relaxation dynamics of a real system.

Apart from the just mentioned problem on the applicability of the MCT equations, there is, however, a much more important one, namely the fact that the MCT equations, as presented here, predict a divergence of the relaxation time at a finite temperature. In Sec. 2 we have seen that there is experimental evidence that there does indeed exists a finite temperature at which $\tau$ diverges, the Vogel temperature $T_0$ (see Eq. (2.1)), which is close to the Kauzmann temperature $T_K$ in which thermodynamic quantities seem to indicate a transition (see Fig. 3). However, in experiments it is found that the divergence of $\tau$ close to $T_0$ is given by the Vogel-Fulcher law, Eq. (2.1), and not by a power-law as predicted by MCT. Thus this is evidence that one should probably not identify $T_0$ with $T_c$. Furthermore the exact calculations for the mean-field models have shown that these models do indeed have two transitions. A thermodynamic one at low temperature $T_s$ and a dynamic one at a higher temperature $T_D$. This latter transition is due to the fact that at $T_D$ the configuration space splits up into domains that are separated by infinitely high barriers. If we recall that the MCT equations for these spin models describe the ergodic $\rightarrow$ non-ergodic transition at $T_D$, we thus are tempted to make the analogy that the Kauzmann temperature of structural glasses corresponds to the temperature $T_s$ in spin glasses and that the $T_c$ corresponds to the temperature $T_D$. Since real systems are not mean-field, the mentioned barriers that are present the mean-field models are no longer infinite and hence there is no longer a sharp transition. Instead one can expect that close to $T_c$ the dynamics changes from a flow-like one, to one in which a few particles hop in a cooperative way over local barriers and recent investigation on the properties of the landscape of supercooled liquids have given evidence that this is indeed the case. Hence we come to the conclusion that the sharp transition predicted by MCT at $T_c$ is avoided and one finds instead only a change of the transport mechanism for the particles. Depending on the system, this change may be very pronounced, such as in colloidal suspension where close to $T_c$ (or in that case close to the critical packing fraction of the particles) the relaxation times become macroscopically large, or only relatively mild, such as in the case of strong glass-forming liquids (silica, $\text{B}_2\text{O}_3$, glycerol) were only a relatively mild change occurs.

It is of course a legitimate question to ask whether or not MCT is indeed not able to describe the relaxation dynamics also below $T_c$. In principle the Mori-Zwanzig formalism allows to obtain also equations of motion for that situation and the “only” thing one has to do is to take into account further slow variables. The result of such a calculation are equations of motion in which the memory function has a somewhat more complicated form, and these equations are usually called “generalized MCT equations” or “MCT-equations including the hopping terms” since they include the ergodicity restoring hopping terms (or at least some of these terms) (see also Ref. [147]). However, so far it has not been possible to come up with an explicit expression for this memory function, i.e. one that does not depend strongly on the approximations that one is forced to make. Therefore only the qualitative form of this generalized memory function is known and if one wants to use these equations of motion to describe, e.g., real data for $F(q,t)$, quite a few fit parameters are left. Despite this difficulty it is, however, possible to make at least some predictions that should be valid independently of the functional form of the generalized memory function. The most important one is that the sharp
transition at \( T_c \) no longer exists and that instead there is a cross-over from a power-law dependence above \( T_c \) to a weaker \( T \)-dependence (e.g. Arrhenius) below \( T_c \). Depending on the strength of the "hopping parameters" in the generalized equations, this transition can be very sharp, or very smooth which allows to distinguish between fragile and strong glass formers. Furthermore it can be shown that despite the presence of the hopping processes, the factorization property of the \( \beta \)-relaxation regime still holds, although in a somewhat different form as the one given by Eq. (3.24) \[143, 144\]. Thus we see that even if our current ignorance of the exact form of the generalized MCT-equations does not allow to make a quantitative comparison between the prediction of the theory and the real data, certain qualitative checks are still possible. In the past such tests have indeed been made \[147, 148\] and it has been found that the theory does indeed allow to rationalize some of the dynamical properties of glass forming liquids also at temperatures below \( T_c \).

Thus we can conclude that the theory is able to give a good description of the relaxation dynamics not only above \( T_c \) but is also a useful theory in a certain temperature range below \( T_c \). In that sense MCT is a very valuable theoretical contribution that has helped to understand the relaxation dynamics of glass-forming liquids at intermediate temperatures \[14\]. In this \( T \)-range the theory has identified the existence of a cross-over in the transport mechanism of the particles with many interesting and universal features. Nevertheless, to what extend the theory is also able to give a correct description of the relaxation dynamics of atomic liquids at temperatures at which the viscosity is much higher, is presently not really known and the focus of current research.

4 Computer Simulations of glass-forming Systems

As we have already mentioned in the introduction, computer simulations are one of the important tools to investigate the properties of glass-forming systems. The goal of this section is therefore to discuss this method in some detail. However, in the following we are not going to give a general introduction to computer simulations since a much more extended coverage can be found in several excellent textbooks \[151, 152, 153, 154, 155, 156\]. Instead we will discuss mainly some of the technical issues of such simulations that are of particular importance for glass-forming systems. But even with this restriction the field is still vast to give a comprehensive review and therefore we will leave out almost completely important topics like the simulation of spin glasses etc. and focus instead on structural glasses.

Roughly speaking there are two broad classes of simulations: Molecular dynamics simulations and Monte Carlo simulations, and in the following we will discuss these two methods in somewhat more detail.

In a molecular dynamics (MD) simulation one tries to solve Newton’s equations of motion for the system of interest and thus to obtain the trajectory of the particles in configuration space. From these trajectories many properties of the system can be directly calculated, at least in principle. The problem with MD is that the known numerical methods to solve these equations work only reliably for a time scale that is significantly smaller (\( O(10^{-2}) \)) than the shortest typical time scale of the system, which in a liquid is given by the local motion of the particles and hence is on the order of 0.1ps. One well known example for such an algorithm is due to Verlet and is given by:

\[
\begin{align*}
\mathbf{r}_i(t + h) &= \mathbf{r}_i(t) + h \mathbf{v}_i(t) + \frac{h^2}{2} \mathbf{F}_i(t) \\
\mathbf{v}_i(t + h) &= \mathbf{v}_i(t) + \frac{h}{2} [\mathbf{F}_i(t) + \mathbf{F}_i(t + h)]
\end{align*}
\]

Here \( \mathbf{r}_i(t) \) and \( \mathbf{v}_i(t) \) are the position and velocity of particle \( i \) at time \( t \), \( \mathbf{F}_i \) is the force acting on this particle, and \( h \) is the time step which for typical liquids has to be on the order of 1fs. In Sec. 2 we

\[\text{Note that in experiments of glass-forming liquids with strong or intermediate fragility it is often found that } T_c \text{ is } 20\%–30\% \text{ above } T_g. \text{ For the strong glass former silica there is evidence from simulations and experiments that that } T_c \text{ is even a factor of two higher than } T_g. \text{ In view of these results it is therefore more appropriate to say that the theory works well at temperatures in which the viscosity has values between } 10^{-1} \text{Poise and } 10^4 \text{Poise.} \]
have seen that upon cooling the relaxation time of a glass-forming liquid increases by 12-15 decades in time. Thus if one wants to investigate this slowing down by means of a simulation it would be necessary to propagate the system by means of Eq. \( 4.12 \) by the same number of decades, which is currently completely impossible even for systems that are as small as 100 particles. The best one can presently do is to simulate a system with \( O(1000) \) particles for \( O(10^6) \) time steps, but most present day simulations cover less than \( 10^7 \) time steps since usually one has to do many independent runs to improve the statistics, to investigate different temperatures, to average (in spin glasses) over different realizations of disorder, etc., all of which together usually takes many years of single processor CPU time. Hence we recognize that one of the major problems in the simulation of glass-forming systems is the huge time range that should be covered. Note, however, that the propagation of the system in its configuration space is so slow because the dynamics of the particles is real.

In a Monte Carlo simulation this drawback does, at least in principle, no longer exist. Since in this method the only rule that has to be obeyed is the one of detailed balance, i.e. the fact that \( w(s \to s') \), the transition probabilities for the propagation of the system from an arbitrary state \( s \) to another arbitrary state \( s' \), fulfill the relation \( w(s \to s') \exp(-\beta(H(s) - H(s')))/w(s' \to s) = \exp(-\beta H(s))/\exp(-\beta H(s')) \), where \( \beta = 1/k_BT \) and \( H(s) \) is the value of the Hamiltonian at state \( s \), a clever choice of the function \( w(s \to s') \) will allow to equilibrate the system also at low temperatures. Unfortunately this is true only in principle. So far it has not been possible to find a updating scheme that allows to equilibrate an arbitrary off lattice system also at low temperatures. For certain special cases we do, however, have algorithms that allow to do this, e.g. systems of hard disks or binary mixtures of particles with very similar radii [157, 158]. For other models it is possible to come up with algorithms that allow at least to probe the system (in equilibrium!) at relatively low temperatures, such as, e.g. the parallel tempering method [159, 160, 161, 162, 163, 164, 165, 166]. Despite this progress one is still quite far away from the ultimate goal: To have a robust algorithm that is able to equilibrate a large class of glass-forming systems (having a substantial number of particles) also at very low temperatures.

Since so far it is not possible to simulate reasonably sized systems over very large time, and since we have seen that with decreasing temperature the relaxation times of glass-forming systems increase rapidly, it is presently difficult to use computer simulations to investigate the equilibrium properties of such systems at low \( T \). What does “low” mean? As mentioned above the length of a typical run is presently around \( 10^7 \) time steps. With a step size \( h \) of a few fs, this gives a total length of 10-50ns which corresponds to about \( 10^2 \)Poise. Using Fig. 2 we thus recognize that present day simulations are just barely able to see the upturn in the \( \eta(T) \) curves seen experimentally in fragile liquids.

Of course one might be tempted to circumvent this problem by making a relatively rapid quench to low temperatures, “anneal” the system for some time, and then to start to measure the properties of the system (structure, diffusion constant, relaxation dynamics, etc.). Although such an approach sounds quite reasonable, a systematic investigation of such a protocol shows that the so obtained results have very little to do with the ones of the system in true equilibrium and therefore should not be done. To demonstrate this one can, e.g., investigate the time-dependence of the intermediate scattering function \( F_s(q,t) \) (see Eq. \( 3.14 \)) after such a quench. In equilibrium \( F_s(q,t) \) depends only on the time difference \( t \), i.e.

\[
F_s(q,t) = \langle \rho_s(q,t)\rho^*_s(q,0) \rangle = \langle \rho_s(q,t+\tau)\rho^*_s(q,\tau) \rangle . \tag{4.3}
\]

In the out-of-equilibrium case the second equality does no longer hold and therefore it is necessary to keep track of both time arguments \( t \) and \( \tau \), e.g., we have to generalize \( F_s(q,t) \) to the function

\[
C_s(q,t_w+\tau,t_w) = \langle \rho_s(q,t_w+\tau)\rho_s(q,t_w) \rangle , \tag{4.4}
\]

where \( t_w \) is the so-called “waiting time”, i.e. the time span between the start of the measurement and the time at which the system has been driven out of equilibrium. In Fig. 3 we show the time dependence of a \( C_s(q,t_w+\tau,t_w) \) for a binary Lennard-Jones system that at time zero has been quenched from a
Fig. 9. Main figure: Time dependence of the correlation function $C_s(q, t_w + \tau, t_w)$ defined in Eq. (4.4) for a binary Lennard-Jones mixture that has been quenched from a temperature $T_i = 5.0$ to a temperature $T_f = 0.4$. The different curves correspond to the stated waiting times $t_w$. Inset: The same data in a log-log plot showing that at long times the correlator shows a power-law dependence on time. Adapted from Ref. [167].

relatively high temperature to a low temperature [167]. The different curves correspond to different waiting times $t_w$. We see that, in contrast of the situation in equilibrium, the relaxation dynamics of the system depends strongly on the waiting time in that the dynamics slows down for increasing $t_w$. One thus says that the system is “aging”. Although the existence of this phenomenon has been known since quite some time [174], it is only in recent years that attempts have been made to describe it by means of statistical mechanics concepts [168, 169, 170, 171, 172, 173, 174, 175, 176]. Note that the figure shows not only that the typical time scale for the decay of the correlation function depends on $t_w$, but also that the shape of the function has changed, since (see inset) it is compatible with a power-law whereas in equilibrium it can be approximated well by a KWW-function (see Sec. 2). Hence we conclude that for the investigation of the *equilibrium* dynamics of a slowly relaxing system it is most important to check carefully that one has indeed reached equilibrium. Note that experience has shown that time correlation functions are much more sensitive to out-of-equilibrium effects than static quantities. This can be understood by recalling that most static quantities show only a very weak $T$-dependence, whereas dynamical observables show a very strong one (see Sec. 3). Therefore in most cases it is not advisable to monitor just quantities like the energy, pressure etc. in order to check whether or not a system has reached equilibrium. Much more useful are the time correlation functions like the one defined in Eq. (4.4) or the function that is the analogous generalization of the mean-squared displacement.

For the case of second order phase transitions it is well known that the static as well as dynamic properties of the systems depend strongly on the size of the system [177]. For the case of structural glasses such dependencies are much less pronounced, although they are present. In Fig. 10 we show the partial static structure factor for the O-O correlation in SiO$_2$ [178]. The solid and dashed curves correspond to the system sizes $N = 336$ and $N = 8016$ atoms and we see that within the accuracy of our data there is no difference between the two data sets. However, in other cases one does indeed find differences in structural properties, e.g. in the distribution of the angles between three neighboring particles in systems like Al-Ca-Si-O, if the system size is below a few hundred atoms [177]. Much more sensitive to system size is the relaxation dynamics. In Fig. 11 we plot the intermediate scattering function for the system sizes shown in the previous figure. From this graph we recognize that the relaxation dynamics is significantly slower than the one for the larger system and that also the shape of the curves close to the plateau are not the same [178]. It has been shown that with decreasing system
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Fig. 10. Partial structure factor for the O-O correlation in amorphous SiO$_2$ at the density 2.36g/cm$^3$. The two curves correspond to two system sizes (box size 16.8Å and 48.37Å). It is clear that within the accuracy of the data no difference is seen.

Fig. 11. Time dependence of the intermediate scattering function of SiO$_2$ at 3760 K. The curves correspond to different system sizes and they demonstrate that the relaxation dynamics in small systems is slower than the one in large systems. Inset: Enlargement of the region close to the plateau.

size and decreasing temperature this difference in the dynamics can become very pronounced in that for $N = 100$ atoms the system takes orders of magnitude longer to relax than the relaxation time for large systems [178, 179, 180]. Although the reason for this strong dependence is not understood very well it is likely related to the fact that in small systems the connectivity of the accessible configuration space is effectively smaller than in larger systems, since in the latter fluctuations in density etc. can be present that are strongly suppressed in the former. Note that exactly the opposite is the case for the case of spin glasses: There one finds that the smaller systems relax faster than the large ones, at least if the interaction range is not too short ranged [181, 182, 183, 184].

As already discussed in Sec. 2, the glass transition is basically just a kinetic phenomenon since it occurs at that temperature at which the typical relaxation time of the system becomes comparable
Fig. 12. Density of SiO$_2$ at $T = 0$ and zero pressure as a function of the cooling rate with which the glass has been produced.

with the time scale of the experiment (such as the inverse of the cooling rate). This effect should not be forgotten if one uses simulations to investigate the properties of glasses, since these will in general depend quite substantially on the cooling rate. As an example we show in Fig. 12 how in the case of SiO$_2$ the density at low temperatures depends on the cooling rate $\gamma$ [70]. (Note that these quenches have been done at constant pressure.) From the figure we recognize that $\rho_f$ does indeed depend significantly on $\gamma$ and that it is far from obvious how this function should be extrapolated to the cooling rates that are typically used in a real experiment (10K/s). The density is a quantity that is relatively benign since it averages over the whole microscopic structure. More microscopic structural quantities, such as the structure factor, local coordination numbers, etc., show a even more pronounced $\gamma$-dependence [70]. Since in general it is not known how the dependence of such quantities on $\gamma$ has to be extrapolated to experimental cooling rates, a comparison with experimental data becomes difficult or even impossible. (But of course many people sweep all these methodological difficulties under the rug and go on to compare happily their results with experimental data.)

Above we have commented on the observation that structural properties of glasses are relatively insensitive to finite size effects once the system is larger than a few hundred particles. There are, however, situations were substantially larger systems are necessary. E.g. in recent years a significant experimental and theoretical effort has been made to understand the nature of the boson peak, mentioned in Sec. 2 (see Fig. 3) [42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56]. Since this peak is an excess in $g(\nu)$, the vibrational density of states, over the Debye-level, $g(\nu) \propto \nu^2$, it is reasonable to plot the density of state divided by $\nu^2$ in order to see whether or not an excess is seen. Note that in a simulation $g(\nu)$ can be calculated from the the eigenvalues of the dynamical matrix or by the time Fourier transform of the velocity-auto-correlation function [185]. In Fig. 13 we show $g(\nu)/\nu^2$ as a function of the frequency $\nu$ and we do indeed see a peak at around $\nu \approx 1.5$THz [186]. However, the plot also makes very clear that the location as well as the height of the peak depends on the size of the simulation box as well as on the cooling rate with which the glass has been produced. Also note that for a sufficiently large system $g(\nu)/\nu^2$ should show at small frequencies a plateau, the Debye-limit. The graph demonstrates however, that even a system with more than 8000 ions is not sufficiently large to show this Debye-law. Hence great care has to be taken if one starts to analyse the modes and the mechanisms that give rise to the observed peak, since it might very well be that one analyses modes that in a realistically large system are irrelevant.

Before we end this section we briefly make some general comments on the systems one simulates.
Roughly speaking one can distinguish two types of simulations: In the first type one tries to obtain some general understanding of the properties of glass-forming systems that subsequently can be used to check theoretical concepts or theories (properties of the energy landscape, applicability of MCT, search for diverging length scales, etc.). In such simulations one does not really care whether or not the simulated system exists also in reality, as long as the model does not have any pathological features. Therefore one often uses very simple models such as lattice gases, Lennard-Jones fluids, spin systems on a lattice, etc. This is in contrast to the situation in which one uses a simulation to understand a particular feature of a given material. In that case it is necessary to consider models that are much more realistic since otherwise the feature of interest might even be completely absent in the simulation (e.g., it is not possible to study the process responsible for the light scattering mechanism by using a simple Lennard-Jones model since there are no polarization effects). The extreme limit of such a realistic calculation would of course be to solve the Schrödinger equation for the many-body problem, but of course it is clear that this is computationally not possible. The best thing one presently can do is to make a so-called \textit{ab initio} calculation in which the particles obey Newton’s equation of motion with a force field that is calculated directly from the wave-function of the system [187, 188]. Such calculations are presently feasible for systems of $O(100)$ particles and time scales of 10ps. As we have seen above, these sizes and time scales are for most cases insufficient and therefore one makes often the further approximation to use \textit{effective} force field that are just the sum of a pairwise interaction potential between the particles. (Sometimes one takes into account also three-body interactions.) These potentials will depend on certain parameters (particle size, effective charges, etc.) that are obtained by fitting the potential to the results from \textit{ab initio} calculations or to experimental data. Although the so obtained potentials might in some cases be surprisingly accurate, they are an approximation and thus it might happen that an effective potential that is reliable for one quantity, is not very realistic for another one [189]. Therefore it is very advisable to check critically to what extend the results that are predicted by a simulation with an effective potential depend on this potential. An instructive example for this can be found in Ref. [190], reproduced as Fig. 1 in Ref. [191], where the authors compare the temperature dependence of the diffusion constant for different potential of SiO$_2$. They found that although the structural properties of the various models are quite similar, the relaxation dynamics differs by orders of magnitude! Thus this clearly shows that it is not easy to use simulations to predict the reality.
5 The Relaxation Dynamics of glass-forming Liquids as investigated by Computer Simulations

In the previous sections we have described some of the properties of glass-forming liquids. In the following we will present the results of computer simulations that have been used to investigate these properties as well as to test to what extent the mode-coupling theory of the glass transition is able to describe the relaxation dynamics of these systems. In particular we will discuss two type of systems: A binary Lennard-Jones mixture (BLJM) and silica (SiO$_2$). As we will see, these two systems have very different structural and dynamical properties and therefore it is of interest to see which dynamical features are nevertheless common and can be rationalized by the theory.

Although in this section we will mainly discuss the simulations of the BLJM system and silica, there is a multitude of results for other glass-forming systems, such as hard spheres, soft sphere systems, water, etc. [192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241]. It is found that many of the properties of these latter systems are qualitatively similar to either the BLJM system or to silica. Thus from this point of view we do indeed discuss the salient features of glass-forming liquids and not only the properties of two particular systems.

5.1 Static and dynamic properties of a simple liquid with Newtonian dynamics

In this subsection we will discuss the properties of a simple liquid in its normal and supercooled state. (Note that “simple liquid” means that the interactions are short ranged and pairwise additive [32].) Normally one-component simple liquids are not good glass-formers, since they crystallize rapidly even if they are supercooled only modestly. Therefore one usually considers binary systems since the additional disorder introduced by the different species is sufficient to prevent that the system crystallizes, at least on the time scale of present days computer simulations (O(10$^8$) time steps). One system that seems to have very good glass-forming properties is a binary mixture of Lennard-Jones particles with interactions that were chosen to mimic the system Ni$_{80}$P$_{20}$ [242]. In the BLJM model we have a 80:20 mixture of particles, which in the following we will call A and B particles, that interact via the potential

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6] \quad \text{with} \quad \alpha, \beta \in \{A, B\}$$

(5.1)

The parameters of the potential are given by $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. Hence we use $\sigma_{AA}$ and $\epsilon_{AA}$ as the unit of length and mass, respectively (setting the Boltzmann constant $k_B = 1$). Time will be measured in units of $(m\sigma_{AA}^2/4\epsilon_{AA})^{1/2}$, where $m$ is the mass of the particles. The number of particles used was 1000 and the cubic simulation box had the size $9.4^3$. The equations of motion were integrated by means of the velocity-Verlet algorithm (Eq. (4.2)) using a time step of 0.01 and 0.02 at high ($T > 0$) and low temperatures ($T < 1.0$), respectively.

In Fig. 14 we show the wave-vector dependence of the static structure factor for the A particles at three different values of $T$ [243]. (Note that in a binary system there are three partial structure factors [32].) From this graph we recognize that in the $T-$range considered, the structure does not change significantly. The only effect seen is that a decrease of $T$ gives rise to peaks and minima that are more pronounced. (If the simulation would have been done at constant pressure, also the location of the peaks would show a weak $T-$dependence since the system expands or contracts if the temperature is changed.) Since also the two other partial structure factors do not show a more pronounced $T-$dependence, we conclude that this quantity is indeed rather insensitive to a change in temperature, in agreement with the comments on this in Sec. 4.

Although the structural and thermodynamic properties of the system show only a very mild $T-$dependence, the dynamic properties show a very strong one. To demonstrate this we have included in the figure also the $\alpha-$relaxation time $\tau(T)$ at the three different temperatures (see below for the precise definition of $\tau(T)$). We see that in the temperature range considered this time increases by a factor of more than $10^3$, showing that the dynamic properties of the system do indeed change much faster than the structural ones.
Fig. 14. Wave-vector dependence of the partial structure factor $S_{AA}(q)$ for a mixture of Lennard-Jones particles. The different curves correspond to different temperatures. Also included are the $\alpha$–relaxation times $\tau$.

The relaxation time $\tau$ characterizes the dynamics only on the time scale of the $\alpha$–relaxation, i.e. on the longest time scale of the system. In order to understand the relaxation dynamics also on the other time scales it is useful to consider time correlation functions. One important example for such a correlation function is the mean-squared displacement (MSD) of a tagged particle which is defined by

$$\langle r^2(t) \rangle = \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \langle |r_i(t) - r_i(0)|^2 \rangle.$$

(5.2)

Fig. 15. Time dependence of the mean-squared displacement of the A particles for BLJM system. The curves correspond to different temperatures that are given by $T = 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.50, 0.475, 0.466, \text{and} 0.446$ (from left to right).

In Fig. 15 we show the time dependence of $\langle r^2(t) \rangle$ for the A particles for different temperatures. Let
us start the discussion of the data with the curves for high $T$. For short times we see that $\langle r^2(t) \rangle \propto t^2$, since we are in the ballistic regime mentioned in Sec. 2. Once $\langle r^2(t) \rangle$ is of the order 0.04, i.e. the distance is around 0.2, the time dependence changes over to a power-law with exponent 1.0, i.e. the system is diffusive. This change in the $t$–dependence is due to the collisions of the tagged particles with its neighbors that surround it at $t = 0$. Despite the presence of these neighbors the particle is still able to move away quickly from its initial position, i.e. $\langle r^2(t) \rangle$ increases quickly with time.

Also for low temperatures we see at early times a ballistic behavior. In contrast to the curves for high $T$, the mean squared displacement does at the end of this regime not cross over to the diffusive regime, but instead shows a plateau at intermediate times. This plateau is due to the cage effect mentioned in Sec. 2, i.e. the temporary trapping of the particle by its neighbors. Only for sufficiently long times the particle is able to leave this cage and once it has done so the MSD quickly crosses over to a $t$–dependence that corresponds to a diffusive motion. Note that the height of the plateau is around 0.03, from which is follows that the size of the cage is around 0.17, i.e. it is relatively small compared to the typical nearest neighbor distance which is around 1.0 [24]

The mean squared displacement gives the typical average distance that a tagged particles moves within a time $t$. It is of course also of interest to investigate the distribution of these distances. This can be done by means of the self part of the van Hove function which is defined as [32, 33]:

$$G^s_{\alpha}(r,t) = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle \delta(r - |r_i(t) - r_i(0)|) \rangle . \quad (5.3)$$

Thus we see that $G^s_{\alpha}(r,t)$ is the probability that a particle of type $\alpha$ has moved within the time $t$ exactly a distance $r$ and that $\langle r^2(t) \rangle$ is just the second moment of this distribution. Furthermore we recognize that $G^s_{\alpha}(r,t)$ is nothing else the the space Fourier transform of the incoherent intermediate scattering function defined in Eq. (3.14). In Fig. 16 we show $4\pi r^2 G^s_{\alpha}(r,t)$ for different values of $t$.

(The reason to plot $4\pi r^2 G^s_{\alpha}(r,t)$ instead of $G^s_{\alpha}(r,t)$ is that it is the former that is measured in the simulation and that will enter most theoretical formula, since the system is isotropic.)

From the graph that corresponds to high $T$ we see that at short times the van Hove function is a single peak that moves quickly to the right (its location moves $\propto t^2$). It is found that this peak is just a Gaussian distribution multiplied with $4\pi r^2$. Also for times that are longer than the duration of the ballistic regime, the curve is a Gaussian. Only now the location of the peak moves proportional to $t$, since the dynamics of the particles is diffusive.

For low temperatures and short times the dependence of $G^s_{\alpha}(r,t)$ on $t$ and $r$ is similar to the one at high $T$. Also at very long times the function is again given by a Gaussian. For intermediate times we see however a very different behavior in that the curves for the lower temperature hardly depends on time. Thus we see here directly the cage effect mentioned earlier, i.e. that the particles are trapped by their neighbors. Note, however, that the curves still do depend on time somewhat (although only

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Fig. 16. $r$–dependence of the van Hove function for the A particles in the BLJM at a high and low temperature (panel (a) and (b), respectively). The curves correspond to times $t = 0.32 \cdot 2^n$, $n = 1, \ldots$. 

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weakly). A closer inspection of the data shows that in this time window the shape of the curves does not change and that their time dependence can be written as

\[ G^s_{\alpha}(r, t) = G^c_{\alpha}(r) + H_{\alpha}(r)G(t) \]

which is nothing else than a special case of the factorization property shown in Eq. (3.24). Thus this is a first example that MCT is able to rationalize a non-trivial behavior for this system. Similar results have been found for the distinct part of the van Hove function [244], i.e. the space-time correlation function in which the second index \( i \) in Eq. (5.3) is replaced by another summation index \( j \) [32, 33].

![Fig. 17.](image)

**Fig. 17.** Time dependence of the incoherent intermediate scattering function for different temperatures. The wave-vector corresponds to the location of the main peak in the static structure factor.

The van Hove correlation function is a correlator that is very useful to understand the dynamics of the particles in real space. However, all scattering experiments are done in reciprocal space and hence it is useful to investigate also how the intermediate scattering functions, introduced in Eqs. (3.13) and (3.14), depend on temperature, time and wave-vector. In Fig. 17 we show the \( t \)-dependence of \( F_s(q, t) \) for the A particles [245]. In agreement with the schematic drawing of Fig. 3 we see that at high temperature the correlator decays quickly to zero and a closer inspection of the data shows that this decay is very close to the expected exponential. At low temperature we see the two-step relaxation discussed in the context of Fig. 3. From this figure one clearly sees how strongly the relaxation dynamics depends on temperature. Note that the curves do not show a dip at intermediate times that in Fig. 3 was associated with the boson-peak. The reason for this difference is that liquids that have a structure in which the particles are very closed packed do normally not have a boson-peak. Instead it is a very prominent feature in systems whose structure is given by an open network, such as, e.g., silica. Finally we remark that the \( T \) - and \( t \)-dependence of \( F_s(q, t) \) of the B particles as well as the one of the coherent function \( F(q, t) \) look qualitatively similar to the curves shown in Fig. 17 [245].

Using the time correlation functions just discussed, we can test a further prediction of MCT, the validity of the time-temperature superposition principle (see Eq. (3.31)). For this we can define an \( \alpha \)-relaxation time \( \tau(T) \) by requiring that \( F_s(q, \tau(T)) = e^{-1} \). In Fig. 18 we show the correlators for the different temperatures as a function of \( t/\tau(T) \). We see that we have basically two temperature regimes. At high temperatures the curves fall at long times quite well onto a master curve that is described well by an exponential. The curves at low \( T \) also fall on top of each other, but this time the master curve is a stretched exponential which is included in the figure as well. (Note that the curve for \( T = 0.466 \) (dashed curve) coincides so well with the KWW-function that the former cannot be seen anymore at long rescaled times.) Similar master curves are found for other correlation functions.
and hence we conclude that the prediction of MCT regarding the validity of the TTSP holds for the present system. We also mention that the stretching exponent $\beta$ is relatively large ($\beta = 0.83$). Its value does, however, depend on the correlator considered (different wave-vector or species) and for the present system values as small as 0.5 have been found [245].

From the mean-squared displacement one obtains immediately the diffusion constant $D$ via the Einstein relation $D = \lim_{t \to \infty} \langle r^2(t) \rangle / 6t$. From the intermediate scattering function we have determined the $\alpha$-relaxation time $\tau(T)$. Thus we now can check whether the $T$-dependence of $D$ and $\tau$ is indeed given by the power-law predicted by MCT (see Eq. (3.23)). That this is in fact the case is demonstrated in Fig. 19, which is a log-log plot of $D$ and $\tau^{-1}$ vs. $T - T_c$. We see that at low, but
not too low, temperatures the data does indeed fall on a straight line, i.e. that we have a power-law dependence. Note that we have fixed the value of $T_c$ for all four data sets to $T_c = 0.435$, which shows that such a power-law can be seen using the same critical temperature, as predicted by the theory.

We also note that the values of the exponents $\gamma$ for the two relaxation times are very close to each other (according to MCT they should be the same) but that they differ from the one for the diffusion constant. According to Eq. (3.23) the product $D(T)\tau(T)$ should be a constant if one is close to $T_c$. In the inset of Fig. 13 we show this product (filled circles) and we recognize that it does depend on $T$, but that this dependence is rather mild compared to the one of $D$ or $\tau$. (We also note that if this product is calculated for the stochastic dynamics discussed in Sec. 5.2 it is basically independent of $T$ for high and intermediate temperatures, but shows at low $T$ the same $T$–dependence as the curve for the ND, see the open symbols in the inset.) The reason for this residual $T$–dependence is twofold: First of all the result given by Eq. (3.23) holds only very close to $T_c$. A recent theoretical MCT calculation for a binary system has shown that if one is not extremely close to $T_c$ the product is indeed not constant and it is likely that one reads off from the $D(T)$ and $\tau(T)$ data only an effective exponent [246]. The second reason is that very close to $T_c$ it cannot be expected that the predictions of MCT are valid, since the hopping processes mentioned at the end of Sec. 3 will become important and modify the result given by Eq. (3.23). That such hopping processes are probably present at the two lowest temperatures can be seen in Fig. 19 in that the data points do no longer fall on the straight line for the power-law.

Finally one wonders of course which one of the exponents $\gamma$ is the correct one. Although there is unfortunately no simple answer to this question the general procedure to determine $T_c$ and $\gamma$ (and hence the other exponents $a$ and $b$) is as follows: The exponents $\gamma$ can be determined from the $T$–dependence of the relaxation times of various correlators as well as from the one of the diffusion constant(s). The exponents $a$ and $b$ (or more general the exponent parameter $\lambda$ given in Eq. (3.26) or (3.29)) can be obtained from fitting various time correlation functions (at different temperatures) in the $\beta$–regime with the $\beta$–correlator. Since all these parameters are connected in a one-to-one way to each other, one has to optimize all these fits in a global way. This approach usually allows to obtain reliable values for $\lambda$ and $T_c$. For the present BLJM system it is found that the exponent $\gamma$ should indeed be close to 2.4, i.e. that the values of $\gamma$ as determined from $D$ are not reliable [245, 247, 248, 233]. The reason why $D$ is more likely of not giving the correct exponent are the mentioned hopping processes: It is sufficient that a few percent of the particles hop (leave their cage) to increase the MSD considerably, i.e. these rare events can change the value of $D$ substantially, whereas these type of events affect the average relaxation time only weakly. Hence it must be expected that very close to $T_c$ the diffusion constant is dominated by these hopping processes that are not taken into account by the ideal version of the theory and that therefore the expected $T$–dependence is modified.

All the results that we have discussed so far concern only qualitative tests of MCT. However, in Sec. 3 we have mentioned that in principle it is possible to use the theory also to do a full microscopic calculation of the relaxation dynamics, if the static quantities, such as the structure factor, are known. In the following we will show that such a calculation is indeed possible, at least for the present BLJM system.

From the simulations described above, it is also possible to obtain the wave-vector dependence of the three partial structure factors with high accuracy, i.e. to within 1%. From these $S_{\alpha\beta}(q)$ one can obtain the direct correlation functions, $c_{\alpha\beta}(q)$, which in turn can be used as input to calculate the vertices $V^{(2)}$ and hence the memory function (see Eqs. (3.17) and (3.18)). Hence this allows to obtain the prediction by MCT for the $q$ and $t$– dependence of the intermediate scattering function that can be compared directly with the results of the simulation.

One quantity of interest for such a comparison is the non-ergodicity parameter introduced in Eq. (3.24), i.e. the height of the plateau in the $\beta$–regime. (If the correlator considered is the coherent or incoherent intermediate scattering function, this height is also known as the Debye-Waller and Lamb-Mössbauer-factor, respectively.) In Fig. 20 we show the $q$–dependence of the non-ergodicity parameters for the three partial coherent intermediate scattering functions. The symbols are the results from the simulations [245] and the solid and dashed lines are the predictions of MCT. The dashed line corresponds to the version of the theory in which the vertices $V^{(2)}$ in Eq. (3.24) depend...
only on the structure factor, i.e. the contribution to $V^{(2)}$ from the three-particle correlations $c_3$ are neglected, whereas the solid line corresponds to the case where $c_3$ has been taken into account \cite{247,103}. (Note that the function $c_3(q,k)$ has been determined also directly from the simulation.) From Fig. 20 we recognize that these two versions of the theory give basically the same prediction for the $q$–dependence of the non-ergodicity parameters and hence we can conclude that for this system the effect of $c_3$ is very small, in agreement with the results for a system of soft spheres \cite{249}.

From the figure we also recognize that the agreement between the theoretical curve from the $c_3$–MCT and the data from the simulation is excellent in that also small details are reproduced very well. We emphasize that no fit parameter of any kind has been used to calculate these theoretical curves. Hence we conclude that the theory is indeed able to predict highly non-trivial quantities of the relaxation dynamics with very good accuracy.

Apart from the $q$–dependence of the non-ergodicity parameters it is also quite simple to calculate the value of the critical exponent $\gamma$, which the theory predicts to be 2.34 \cite{247}, in very good agreement with the values 2.4-2.5 found from the simulations. Also the $q$–dependence of the amplitudes $h$ occurring in Eq. (3.24) for the coherent and incoherent scattering function is predicted reliably. The only quantity for which a significant discrepancy between theoretical prediction and simulation is found is the critical temperature $T_c$ for which MCT predicts a value of 0.92 whereas the value from the simulation is 0.435 \cite{247}. Why there is such a large difference and even more puzzling why despite this large difference all the other predictions of the theory are so accurate, is presently not well understood. It has to be mentioned, however, that this observation does not only hold for the present BLJM system but has also been found for the case of hard spheres and of soft spheres \cite{249,250,91}.
Supercooled liquids, the glass transition, and computer simulations

Fig. 21. Time dependence of the coherent and incoherent intermediate scattering function for the A particles. The symbols are the results of the simulation and the solid lines the prediction of MCT. The two wave-vectors correspond to the location of the first maximum and minimum in the static structure factor.

The quantitative tests of the MCT that we have presented so far concerned the dynamics on intermediate and long times, i.e. the time scale of the $\beta-$ and $\alpha-$relaxation. As we have already mentioned in Sec. 3, this dynamics is predicted to be independent of the microscopic dynamics (and below we will give evidence that this is indeed the case). However, if one wants to use the theory to predict the full time dependence of the correlation functions it is necessary to have also a good theory for the relaxation dynamics at short times, i.e. to know the memory function $M_{\text{reg}}$ in Eq. (3.15). As already mentioned in Sec. 3 such a theory does presently not yet exist and therefore one has to content oneself with a phenomenological Ansatz for $M_{\text{reg}}$. One model that has been found to work well is given by

$$M_{\text{reg}} = \alpha(q)/\cosh(\beta(q)t),$$

(5.5)

where $\alpha(q)$ and $\beta(q)$ are constants that can be determined directly from sum rules over static quantities [25, 76, 82, 251]. Using this functional form of $M_{\text{reg}}$, the time and $q-$dependence of the solution of the MCT equations can be obtained numerically. The temperature dependence of these solutions enters only via the $T-$dependence of the static structure factor and trivial kinetic factors. However, as we have mentioned above, the theory overestimates the value of the critical temperature $T_c$ at which the system freezes ($T_{\text{sim}}^c = 0.435$ and $T_{\text{MCT}}^c = 0.92$). This means that close to $T_{\text{sim}}^c$ the value of the vertices in the memory function are already too large. To fix this problem we have evaluated this memory function at a temperature $T_f(T_f)$ and have adjusted $T_f$ such that the time scale for the $\alpha-$relaxation as predicted by the theory for $F_{\text{AA}}(q,t)$ at $q = 7.25$ matched the one of the simulation at temperature $T_f$. More details on this can be found in Refs. [252, 253].

In Fig. 21 we compare the time dependence of the coherent and incoherent intermediate scattering function as obtained from the simulation [245, 254] and as predicted by the theory [252, 253]. The two wave-vectors correspond to the location of the minimum and maximum in the partial structure factor for the A particles. From this figure we recognize that at intermediate and long times the agreement between theory and simulation is very good in that the height of the plateau, the time scale for the $\alpha-$relaxation, as well as the shape of the $\alpha-$relaxation are very similar. The main discrepancies are found for $F_{\text{AA}}(q,t)$ for the larger wave-vector in that at short times the theoretical curve shows a strong oscillation that is not present in the data from the simulation. This difference indicates that the effective damping of the correlator at short times is not described correctly, i.e. that for this value of $q$ the memory function $M_{\text{reg}}$ is too small. We emphasize, however, that this error has nothing to
do with the inadequacy of the MCT but instead is related to our insufficient understanding of the
dynamics of liquids at short times (see also Ref. [255]). In contrast to this the relaxation dynamics of
the system at intermediate and long times is described very well by the theory since similar results
as the ones shown in Fig. [2] are found also for the other partial correlation functions and other
wave-vector [252].

5.2 The relaxation dynamics of a simple liquid with stochastic dynamics

The results discussed in Section 5.1 concerned the static and dynamical properties of a simple liquid
with Newtonian dynamics. However, in quite a few practical applications, such as colloids or polymers
in a solvent, the microscopic dynamics is better described by a Brownian one. The goal of this
subsection is therefore to investigate to what extend the microscopic dynamics influences the relaxation
dynamics, and hence the slowing down of the dynamics upon cooling, in a glass-forming system.

As we have seen in the previous sections, according to mode-coupling theory a small change in
structure can have a large effect on the relaxation dynamics of the system, a result that is compatible
with the curves and relaxation times shown in Fig. [4]. Hence if we want to study the influence of the
microscopic dynamics upon the relaxation dynamics it is imperative not to change the static properties
of the system. One possibility to do this is to use exactly the same interaction potential that we have
used to study the dynamic properties of the BLJM system and to change only the equations of motion.
One alternative to Newton’s equations of motion is a Brownian dynamics in which the inertia term is
neglected and instead one has a friction term as well as an external noise. However, the numerical
integrators that exist for such types of equations are not very accurate and thus require a small step
size [256, 257], which is of course very unpleasant for systems in which the dynamics is slow. One
possibility to circumvent this problem is to use a “stochastic dynamics” (SD), in which the equations
of motion are still second order, but they include also a damping and noise term [257, 248]:

\[ m\ddot{r}_i + \sum_l V_l(|r_i - r_l|) = -\zeta \dot{r}_i + \eta_i(t) \]  

(5.6)

Here \( V_l \) is the potential between particles \( i \) and \( l \), and \( \eta_i(t) \) are Gaussian distributed random variables
with zero mean, i.e., \( \langle \eta_i(t) \rangle = 0 \), and \( \zeta \) is a damping constant. The fluctuation dissipation theorem
relates \( \zeta \) to the second moment of \( \eta_i \), and we have \( \langle \eta_i(t) \cdot \eta_i(t') \rangle = 6k_B T \zeta \delta(t - t') \delta_{il}. \)
For the following we will use a value of \( \zeta \) of 10, which is large enough that the results presented do not depend on \( \zeta \)
anymore (apart from a trivial shift in the time scale). More details on this simulation can be found in
[133, 243]. Note that all the static properties of the system are completely independent of the value
of \( \zeta \) and that \( \zeta = 0 \) corresponds to the case of the Newtonian dynamics.

In Fig. [22] we show the time dependence of the intermediate scattering function as obtained from the
SD (solid lines). The wave-vector is 7.20, i.e. is the location of the maximum in the static structure
factor. Although at a first glance the set of curves look quite similar to the ones found for the
Newtonian dynamics (ND), see Fig. [17] there are important differences. To simplify their discussion
we have included in the figure also the data from the latter dynamics at certain temperatures (dashed
lines). Comparing the corresponding data at the highest temperature, we see that the curve for the ND
decays quicker to zero than the one for the SD and that the relaxation time, which can, e.g., be defined
again via \( F_s(q, \tau) = e^{-1} \), is about 7 times shorter. For the lowest temperature considered, this ratio has
grown to about 30. At these temperatures all curves show the plateau of the \( \beta \)-relaxation. However,
the correlators for the ND approach this plateau very quickly whereas the ones for the D approach it
very smoothly. Thus we conclude that the way the particles explore the cage is very different. Despite
from these differences there are, however, also quite a few similarities in the correlators from the two
types of dynamics: First of all the height of the plateau seems to be the same. This means that the
size of the cage is independent of the microscopic dynamics (see also Ref. [258]). Furthermore also
the shape of the correlator in the \( \alpha \)-regime is independent of the dynamics as can be concluded from
the fact that for certain temperatures the dashed and solid curves trace each other very well and
the fact that at low \( T \) this shape is independent of \( T \) (see Fig. [18]). These results are in agreement
with the prediction of MCT since the theory does indeed predict that the relaxation dynamics at
Fig. 22. Time dependence of the incoherent intermediate scattering function for the A particles. The solid lines are for the case of the stochastic dynamics at the temperatures \( T = 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.5, 0.475, 0.466, 0.452, \) and 0.446. and the dashed lines are for the Newtonian dynamics at \( T = 5.0, 0.466, \) and 0.446. The dashed-dotted lines is a fit to the SD curve at \( T = 0.446 \) with the \( \beta \)–correlator from the MCT.

Intermediate and long times is independent of the microscopic dynamics that is characterized by the memory function \( M^{\text{reg}}(q, t) \) in Eq. (3.15).

Also included in the figure is a fit to the SD curve at the lowest temperature with the \( \beta \)–correlator given by Eq. (3.25) (dashed-dotted curve). The value of \( \lambda \) was fixed to 0.708, the value that MCT predicts for this system \(^{247}\) and is hence not a fit parameter. (We mention that in order to get reliable fits it was necessary to include also the correction to the \( \beta \)–correlator, which according to MCT are of the form \( t^{26} \) \(^{13}\) (see also Refs. \(^{243},^{259},^{260}\) for more details.) The figure shows that this functional form gives a very good fit to the data for more than three decades in time, which is strong evidence that MCT does indeed give a reliable description of the \( \beta \)–relaxation.

Fig. 23. Temperature dependence of the relaxation time \( \tau \) as determined from the incoherent intermediate scattering function and the diffusion constant (in both cases for the A particles). The filled and open symbols correspond to the Newtonian and stochastic dynamics, respectively. The straight lines are fits with a power-law using \( T_c = 0.435 \) as the critical temperature. From Ref. \(^{243}\).
From the intermediate scattering function and the mean-squared displacement of a tagged particle one can now determine again the relaxation time $\tau(q, T)$ and a diffusion constant. According to MCT the $T$ dependence of these quantities should be the same as their $T$–dependence for the case of the ND. That this is indeed the case is shown in Fig. 23 were we plot $D$ and $\tau^{-1}$ for the two types of dynamics. The value of the critical temperature $T_c$ has again been fixed to $T_c = 0.435$, the value we have found for the ND. The plot shows that with this value of $T_c$ also the data for the SD are rectified for 2-3 decades in $D$ (or $\tau^{-1}$). Hence we conclude that the power-law given by Eq. (3.23) is found also for the SD. Moreover, the exponents $\gamma$, given by the slope of the straight lines, seems basically to be independent of the microscopic dynamics. In particular the values of $\gamma$ as determined from $\tau(T)$ are the same within the accuracy of the data. Hence we conclude from this figure and the previous one that the whole $\alpha$–process is independent of the microscopic dynamics, apart from an overall shift in the time scale, a result that is rather surprising. From Fig. 22 we recognize that this shift is only due to the different time dependence of the dynamics at short times, i.e. by the different choice of $M^{\text{reg}}(q, t)$. Since we have shown in Fig. 21 that MCT is able to give a correct description of the relaxation dynamics at long times, we hence conclude that if we would have a reliable theory for the short time dynamics, we would be able to describe the relaxation dynamics in the whole time range and for all microscopic dynamics. (Of course this has to be restricted to the case that the microscopic dynamics is “local”, i.e. we do not allow, e.g., global Monte Carlo moves \[153, 154, 156\].)

**Fig. 24.** Main figure: Time dependence of $R_l(t)$ as defined in Eq. (5.7) using various correlators (see main text for details). The time dependence of these correlators are shown in the inset.

The last feature of the relaxation dynamics that we want to discuss is the factorization property given in Eq. (3.24). Recall that this equation says that on the time scale of the $\beta$–relaxation the shape of all time correlation function is the same. In order to check whether this is indeed true one could make fits to each of the correlation functions with the $\beta$–correlator using the same value of $\lambda$, as it has been done in Fig. 22. Since this procedure is quite involved it is, however, more advisable to use an approach that has been proposed some time ago by Signorini et al. \[197\] and which goes as follows: Let $\Phi_l(t)$ be an arbitrary correlator. From Eq. (3.24) it thus follows that the following ratio is independent of $l$:

$$R_l(t) = \frac{\Phi_l(t) - \Phi_l(t')}{{\Phi_l(t'') - \Phi_l(t')}}.$$  \hspace{1cm} (5.7)

Here $t'$ and $t''$ are two arbitrary times in the $\beta$–regime. If Eq. (3.24) does indeed hold, the time dependence of $R_l(t)$ should just be the function $G(t)$, hence be independent of $l$. In Fig. 24 we show the time dependence of $R_l(t)$ for a total of 36 correlators, using times $t' = 200$ and $t'' = 15000$. \[103\]
These correlators include the coherent and incoherent scattering function for the A and B particles at different wave-vectors and their time dependence is shown in the inset of the figure. From this inset we recognize that the time dependence of all these correlators differs strongly in that the height of the plateaus, the stretching etc. covers a wide range of values. From the main figure we see, however, that on the time scale of the $\beta$-relaxation all these curves are indeed very similar in that the rescaling given by Eq. (5.7) makes them to collapse nicely onto a master curve, the shape of which is the function $G(t)$. Hence we can conclude that for this system the factorization property predicted by MCT does indeed hold.

5.3 Static and dynamic properties of a network forming liquid

In the previous two subsections we have discussed the static and dynamic properties of a simple liquid and have shown that this dynamics can be rationalized very well with the help of MCT. The structure of these simple liquids is quite close to the one of a close packing of hard spheres. Already in Sec. 2 we have mentioned, however, that the so-called strong glass-formers have a structure that is often quite open and that the $t$-dependence of their relaxation dynamics is, by definition, close to an Arrhenius law. Hence it is legitimate to ask whether MCT is a useful theory for these type of systems as well. The goal of this section is therefore to discuss the results of some computer simulations that have been done to address this question.

In order to make a computer simulation of a strong glass-former it is of course necessary to have an interaction model that has indeed the required properties, i.e. an Arrhenius dependence of the relaxation times. Fortunately silica, the paradigm of a strong glass-former, is an important material not only for fundamental science but also in technical applications as well as fields like geology. Therefore there are a multitude of potentials available that claim to give a good description of this material [6, 18]. One of the potentials that does indeed seem to be quite reliable has been proposed some time ago by van Beest, Kramer, and van Santen (BKS) [261], and its functional form is given by

$$\phi_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta} \exp\left(-B_{\alpha\beta} r\right) - \frac{C_{\alpha\beta}}{r^6}, \quad \alpha, \beta \in [\text{Si, O}],$$

(5.8)

where $r$ is the distance between the ions of type $\alpha$ and $\beta$. The values of the constants $q_\alpha, q_\beta, A_{\alpha\beta}, B_{\alpha\beta},$ and $C_{\alpha\beta}$ can be found in Ref. [261]. Due to the presence of the Coulomb interactions it is necessary to use an Ewald summation technique to calculate the forces [153, 154], or one of the equivalent methods proposed more recently [262, 263, 264]. Therefore making a simulation of these type of systems are presently about 10 times more expensive in computer time that models with only short range interactions. As mentioned in Sec. 4 it is sometimes necessary to use relatively large systems in order to avoid finite size effects in the dynamics [178, 179]. Therefore the following results have been obtained for a system size of about 8000 atoms, which corresponds to a box size of around 50 Å. More details of the simulation can be found in Refs. [142, 148].

Since we are modeling silica, e.g. a material that really exists in nature, it is possible to compare the results from the simulation with real experimental data (and in fact this should always be done in order to check whether the potential used is indeed reliable, i.e. compatible with known experimental facts). One such comparison is shown in Fig. 25, were we compare $S_n(q)$, the static structure factor as measured in a neutron scattering experiment, from the simulation with real experimental data. This function can be easily calculated from the three partial structure factors $S_{\alpha\beta}(q)$ using the relation

$$S_n(q) = \frac{1}{N_{\text{Si}} b_{\text{Si}}^2 + N_{\text{O}} b_{\text{O}}^2} \sum_{\alpha,\beta} b_\alpha b_\beta S_{\alpha\beta}(q),$$

(5.9)

where $b_\alpha$ are the neutron scattering length whose experimental values can be found in the literature [261]. From the figure we see that the agreement between the experiment and the simulation is
good, which shows that the BKS potential is quite reliable. Hence we can have some confidence that the dynamical properties as predicted by the model will not be too far off from the ones of real silica.

In Fig. 26 we show the $T$-dependence of the diffusion constants for the Si and O atoms (which were determined using the Einstein relation) \[143\]. Note that the temperature scale covered is $6100 \, \text{K} \leq T \leq 2750 \, \text{K}$, i.e. the temperatures are rather high. The reason for this is that silica is a very viscous system even at high temperatures (the relaxation time at 2750 K is around 10ns, see also Fig. 3) and hence it is presently not possible to equilibrate the system in a simulation at significantly lower temperature. From the figure we recognize that at low temperatures the diffusion constants show an Arrhenius dependence, as can be expected for this system (see bold solid lines). The activation energies, given in the figure, agree well with the experimental values \[272, 273\]. Hence we conclude that the BKS potential is indeed able to give also a satisfactory description of the relaxation dynamics of real silica.

What is surprising in the data from the simulation is that at high temperatures there is a crossover from the Arrhenius dependence of $D$ to a weaker one, i.e. there is a significant bend in the curves. (Note that the viscosity and the relaxation times determined from the intermediate scattering functions shows a very similar $T$-dependence, hence this non-Arrhenius behavior is not a particularity of the diffusion constant.) Such a $T$-dependence is reminiscent to the behavior found in fragile liquids close to the critical temperature of MCT. Therefore it is reasonable to check whether the power-law predicted by the theory, see Eq. (3.23), can also in this case be used to rationalize the data. That this is indeed possible is demonstrated by the two dashed lines shown in the figure that represent such a power-law dependence. If one assumes that the value of $T_c$ is the same for Si and O, the resulting critical exponents $\gamma$ are indeed very close together, in agreement with the prediction of the theory.

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A brief comment on the meaning of the various peaks: In a simple liquid, see e.g. Fig. 14, the first main peak corresponds to the length scale of a nearest neighbor. However, for ionic systems like silica this identification is not necessarily true, since the charged atoms will induce a local ordering of the system. In the case of SiO$_2$ this is done in the form of tetrahedra, i.e. a silicon atom is surrounded by four oxygen atoms. These tetrahedra are connected via their corners and form an irregular open network. Thus in this system the first peak at in the structure factor (located at 1.6$\,\text{Å}^{-1}$) does not correspond to the nearest neighbor distance (which would be a Si-O pair) but to the distance between two neighboring tetrahedra. For even more complex systems, like Na$_2$O-SiO$_2$, one can have structural features at even larger length scales \[267, 268, 269, 59, 270, 271\].
Also the $\alpha$-relaxation times $\tau(T)$ show a power-law dependence and the critical temperature is the same as the one found for the diffusion constant. However, as it was already the case for the BLJM system, the value of the critical exponent $\gamma$ as determined from $\tau$ is larger than the one found for $D$ ($\gamma_\tau = 2.45$) [148].

The critical temperature $T_c$ is found to be around 3330 K, a value that is far above the melting temperature of the system ($T_m \approx 2000$ K). Thus we see that the critical temperature of MCT has nothing to do with the system being in a supercooled state. Instead it is just a temperature at which the transport mechanism of the atoms changes, as already discussed in Sec. 3. Last not least we mention that Hess et al. have used experimental data for the viscosity to estimate $T_c$ and have predicted a value around 3200 K [149, 150], in surprisingly good agreement with the estimate from the simulation.

That MCT is not only able to rationalize some feature of the relaxation dynamics of the $\alpha$-relaxation but also in the $\beta$-regime is shown in Fig. 27 were we plot the functions $R_i(t)$ defined in Eq. (5.7). The correlators used to calculate these curves are the incoherent intermediate scattering function for Si and O at $q = 1.7, 2.2, 2.8, 4.43, 5.02$ and $5.31$ Å$^{-1}$, but other correlators can be included as well [274]. As it was the case of the BLJM system, we see that in the $\beta$-regime the curves fall on top of each other. In agreement with the prediction of MCT, the range where a master curve is found expands if the temperature is lowered (compare the two panels). The shape of the master curve is given by the $\beta$-correlator $g_\beta(t)$ from which one can determine the exponent parameter $\lambda$. Using this value of $\lambda$ (= 0.713), one can use Eqs. (3.29) and (3.30) to calculate the theoretical value of the critical exponent $\gamma$, which turns out to be 2.35, in very good agreement with the real value, which is around 2.45.

As it was already the case for the BLJM system it is important to understand also for this network-forming glass whether MCT is able to give only a qualitative description of the relaxation dynamics, or whether it is also possible to make a quantitative calculation. It is found that if one uses the expressions given by Eq. (3.18) for the vertex $V^{(2)}$ there is no good agreement between, e.g., the wave-vector dependence of the non-ergodicity as predicted by the theory and the one found in the simulation [253, 103]. This is seen in Fig. 28 where we compare the result from the simulation (circles) with the ones of MCT (dashed lines). However, we have already mentioned in Sec. 3, that there are also contributions to the vertices $V^{(3)}$ that are related to the three-particles correlation function.
Fig. 27. Time dependence of the functions \( R_l(t) \) as defined in Eq. (5.7) for the case of silica. The upper and lower panel corresponds to \( T = 4000 \text{ K} \) and \( T = 2750 \text{ K} \), respectively. The correlators used are \( F_s(q, t) \) for silicon and oxygen at \( q = 1.7, 2.2, 2.8, 4.43, 5.02 \) and \( 5.31 \text{ Å}^{-1} \). The times \( t'' \) and \( t' \) are 0.4 ps and 1.6 ps for \( T = 4000 \text{ K} \) and 11 ps and 106 ps for \( T = 2750 \text{ K} \), respectively.

c\(_3\)(\(q, k\)). For the case of the BLJM system we have found, see Fig. 20, that these contributions do not change significantly the value of the non-ergodicity parameter. For a network-forming liquid like silica this is, however, no longer the case in that there is a quite large difference between the theoretical prediction in which \( c_3 \) is neglected and the one in which \( c_3 \) is taken into account. This can be seen, e.g., in Fig. 28 where we have included also the curve from the MCT in which the \( c_3 \) terms are included (solid line). We find that the curve with and without these terms differ significantly in that the former is quite a bit lower than the latter one, in particular at intermediate and large wave-vectors. In addition we recognize that the inclusion of the inclusion of these terms lead to a much better agreement between the theory and the data of the simulation. For the case of the Si-Si correlation one can even say that the theory makes a very good prediction for this highly non-trivial function. Hence we conclude that also for the case of silica, the prototype of a strong glass-former, the mode-coupling theory is able to rationalize not only some qualitative features of the relaxation dynamics, but also to make quantitative predictions that are surprisingly accurate.

6 Summary and Perspectives

Space and time limits imposed by the (very wise!) editors, and ignorance from my side, have had the effect that many highly interesting and exciting aspects of glassy systems could not be discussed in this review. The simulations done in the context of the recent theoretical developments that seem to indicate a much closer connection between structural glasses, that have no frozen in disorder, and spin glasses, in which the disorder is quenched, could unfortunately not been mentioned. Likewise I had to leave out the discussion of the interesting and promising approach to use the language of “landscapes” (potential and free energy) to describe glassy systems, as well as the fascinating possibility that also driven systems (sheared, stirred, etc.) can be characterized by an effective temperature, thus suggesting a close connection between these systems and aging glasses. All these topics, and many others, will certainly be the focus of much research in the years to come.
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