REVIEW ARTICLE

Computer simulations of supercooled liquids and glasses

Walter Kob

Institut für Physik, Johannes Gutenberg-Universität, Staudinger Weg 7, D-55099 Mainz, Germany

Abstract.   After a brief introduction to the dynamics of supercooled liquids, we discuss some of the advantages and drawbacks of computer simulations of such systems. Subsequently we present the results of computer simulations in which the dynamics of a fragile glass former, a binary Lennard-Jones system, is compared to that of a strong glass former, SiO_2. This comparison gives evidence that the reason for the different temperature dependences of these two types of glass former lies in the transport mechanism for the particles in the vicinity of T_c, the critical temperature of mode-coupling theory. Whereas that for the fragile glass former is described very well by the ideal version of mode-coupling theory, that for the strong glass former is dominated by activated processes. In the last part of the article we review some simulations of glass formers in which the dynamics below the glass transition temperature was investigated. We show that such simulations might help to establish a connection between systems with self-generated disorder (e.g. structural glasses) and quenched disorder (e.g. spin glasses).

1. Introduction

The history of manufactured glasses is several thousand years old [1] and thus it might seem that we have had enough time to gain an excellent understanding of this type of material. A brief glance at the recent literature and the topics of many specialized conferences shows, however, that this is not the case at all. Although a vast amount of detailed knowledge on various properties of all sorts of glasses has been accumulated, and our understanding of these materials has certainly increased tremendously since ancient times, the answers to some of the most basic issues are still a matter of debate. Apart from some questions that have already been posed many years ago, such as regarding the mechanism that gives rise to the glass transition, new questions have emerged very recently, such as that of the nature of the glass transition in small pores, whether or not glasses are dynamically homogeneous or heterogeneous, and how systems with frozen-in disorder (e.g. spin glasses) are related to the ones with self-generated disorder (e.g. structural glasses). Because of the vastness of the field, the present article does not of course even attempt to give an exhaustive review of all of these different topics and developments, and we refer the interested reader to the various textbooks and review articles on such subjects [2–4]. In the following we will therefore focus only on certain topics related to supercooled liquids and glasses. Hence the fact that many other issues will be treated only briefly or not at all should not be viewed as a statement of their irrelevance, but rather as a (somewhat arbitrary) choice of the author.

Computer simulations have of course a much shorter history than glasses, since the first work dates back only to the 1950s [5]. However, it has already been shown that such simulations can be an excellent tool for investigating the properties of complex systems [6], and it can be expected that with the availability of faster and cheaper computers, as well as improved

algorithms, such simulations will play an even more important role in the future than they do now. In this article we will discuss how such simulations can be used to gain insight into the structure and the dynamics of supercooled liquids and glasses. Again, the work on this subject is now far too extensive to be completely covered in this article, and therefore we present only a small, but we hope relevant, subset of it and refer the interested reader to the above-mentioned textbooks [2, 3] and other review articles on this subject [4, 7, 8].

In order to facilitate the reading of the articles for those not familiar with the subject, we will give in section 2 a brief introduction to the field of supercooled liquids and glasses and discuss some of the questions that are currently debated. The following section is then devoted to issues related to computer simulations. In section 4 we will discuss results regarding the *equilibrium* dynamics of fragile and strong glass formers, and at the end show that in the *non-equilibrium* dynamics of glass-forming liquids also many very interesting phenomena occur, which so far are not understood at all, and which can be studied very well by means of computer simulations.

2. Supercooled liquids and glasses

In this section we will briefly review some facts regarding the structure and dynamics of supercooled liquids and glasses. Despite its briefness it should allow the reader to become familiar with some of the issues concerning supercooled liquids and glasses so that the following sections will become more comprehensible. More detailed discussions of these topics can be found in references [2–4].

First of all it is appropriate to specify what we mean in the following by the terms 'supercooled liquids' and 'glass'. The standard point of view is the following: if a liquid can be cooled below its melting temperature T_m without the occurrence of crystallization, it is called a good glass former, and when the temperature is less than T_m the system is called supercooled. The static and dynamical properties of such systems can be studied over a large temperature range below T_m and it is found that their relaxation times increase very quickly by many (12–14) decades if the temperature is lowered. At a certain temperature the relaxation time exceeds the timescale of the experiment and therefore the system will fall out of equilibrium. It is this falling out of equilibrium that is called the glass transition. At temperatures well below this glass transition temperature no relaxation seems to take place any longer (on any reasonable timescale) and it is customary to call this material a glass. (Note that this transition temperature will in general depend on the type of experiment, since its definition involves the timescale of the experiment. This definition should also not be confused with the one often used by experimentalists in which a glass transition temperature is defined as the temperature at which the viscosity of the system has the (somewhat arbitrary) value 10^{13} P.)

In the following we will adopt a point of view regarding the term 'supercooled' which is slightly different and is motivated by the experimental observation that if a system approaches its glass transition temperature its relaxation dynamics becomes non-Debye, i.e. that the time correlation functions decay in a non-exponential way (e.g. they show a two-step relaxation), whereas it shows a Debye behaviour at high temperatures. The reason for this phenomenon will be discussed below. It has been found, however, that, e.g., glycerol and B_2O_3 show this sort of non-Debye behaviour also at temperatures significantly *above* the melting temperature [9, 10]. Therefore one has to conclude that the non-Debye relaxation has nothing to do with the system being supercooled, a point of view which receives support from the theory of the dynamics of dense liquids [11]. In addition, it is not hard to imagine a system that does not crystallize at all, i.e. one for which the concept of a melting temperature, and hence the term 'supercooled', does not even apply (e.g. in atactic polymers). Nevertheless, it can be expected that the dynamics

of such a system will become very slow when the temperature is decreased and that thus the system will undergo a glass transition. For these reasons we will mean in the following by 'supercooled' that the relaxation dynamics of the system is non-exponential and *not* that its temperature is below T_m. Furthermore, in order to simplify the language, we will always use, in the following, temperature as the variable that drives the slowing down of the dynamics. The reader should, however, bear in mind that there are systems in which the glass transition is driven by a change of particle concentration, such as colloids or kinetic lattice gases [12, 13].

If the structural and dynamical properties of a good glass former are measured in the temperature range between the high-temperature regime and the glass transition temperature, one finds that all structural quantities (density, structure factor, etc) and thermodynamic quantities (specific heat, etc) show a very gentle temperature dependence, in that they change by few per cent or a factor of 2–3 [2, 3]. (Note that the experimental observation that the specific heat C_p shows a pronounced drop at the glass transition temperature—see, e.g., reference [14]—does not contradict this statement, since this effect is due to fact that the system falls out of equilibrium, i.e., that certain translational degrees of freedom do not contribute any longer to the specific heat. Thus the drop in C_p is a purely kinetic effect.) As already mentioned above, dynamic quantities, such as the diffusion coefficient D and the viscosity η, will in general show a much more pronounced temperature dependence than thermodynamic quantities. It is this huge variation of the transport coefficients that makes the experimental investigation of the dynamics, and its theoretical description, such an interesting challenge. Phenomenologically, the temperature dependence of the dynamics can be described quite well by the so-called Vogel–Fulcher law

$$\eta \propto \exp(ET_0/(T - T_0))$$

where $T_0 < T_g$ is the so-called Vogel temperature and E is a parameter that determines the shape of the curve. If E is large, the temperature dependence is Arrhenius-like, and if it is small, η shows a pronounced upward bend at a temperature slightly above T_0. Angell coined the terms 'strong' and 'fragile' glass formers for the former and latter cases, respectively [15]. Below, we will discuss how the dynamics of strong and fragile glass formers differ on the microscopic level.

Having discussed some of the phenomena observed in the temperature dependence of glass-forming liquids, it might be useful at this point to make some comments on the various theoretical approaches that have been used to rationalize the dramatic slowing down of the dynamics when the temperature is lowered. One of the simplest potential mechanisms is that whereby, upon cooling, the system approaches the critical point of a second-order phase transition, and hence the increase of the relaxation times just indicates the critical slowing down of the system when the temperature approaches this point. It is generally believed that it is this mechanism that is responsible for the glass transition in spin glasses [4, 16–18]. For structural glasses the situation is much less clear, since the presence of a second-order thermodynamic phase transition implies that one should be able to identify an order parameter or a growing length scale. Since in computer simulations it is relatively easy to measure such an order parameter or length scale, *if one knows what to look for*, they have been used quite extensively to find evidence for the existence of a thermodynamic transition in structural glasses. However, as discussed in detail in reference [19], these efforts have led to no positive results so far.

One of the first successful theories for the glass transition is the one proposed by Gibbs and DiMarzio [20] for dense polymer melts. The basic idea of this theory is that with decreasing temperature the configurational entropy to the polymers decreases and vanishes at a finite temperature, thus leading to the glass transition. Below, we will come back to this theory and discuss it in more depth in the context of some computer simulations that have been performed

to check its validity.

Another very successful theory is the so-called mode-coupling theory (MCT) which has been worked out by Götze, Sjögren, and co-workers [11]. Starting from the theory of dense simple liquids [21] MCT derives equations of motion for time- and wave-vector-dependent correlation functions and makes very detailed predictions on the time and temperature dependence of these quantities when the system is in the supercooled state. As will be discussed below, many of the predictions of this theory have been confirmed in experiments and computer simulations, and thus MCT can currently be regarded as the best available theory of the dynamics of supercooled liquids.

In the following sections we will extensively discuss computer simulations that have been carried out in order to test the validity of the two theories just mentioned. The goal of this discussion is not to give an exhaustive review of all of the possible tests that have been made so far, but rather to present some exemplary results of simulations in order to convince the reader that such simulations can be a very powerful tool for checking to what extent a theory is valid.

3. Computer simulations of glass formers: advantages and drawbacks

The goal of this section is to discuss certain aspects of computer simulations that are particular to simulations of supercooled liquids and glasses. More general introductions to simulations can be found in various textbooks, such as references [6].

The most outstanding advantage of computer simulations is that they provide an extremely large degree of freedom regarding the systems that can be studied. *In principle*, it is no problem to investigate any Hamiltonian that one is interested in, be it on a classical or on a quantum mechanical level. By making a judicious choice of the Hamiltonian considered, it is therefore possible to investigate, e.g., systems in which the dynamics is determined by purely kinetic constraints instead by energetic ones [13, 22, 23], to study molecules or polymers with an exactly specified shape and size [24–27], to investigate the system in thermodynamic states which are difficult to realize experimentally—such as under negative pressures and for high temperatures [28–32], and to study the dependence of the structure and the dynamics of a system in a small pore of a *well-defined* size and shape [33, 34]. For example, simulations of supercooled water have provided evidence that the latter system has a liquid-to-liquid transition [35], and from simulations of SiO_2 novel (crystalline) phases have been predicted [36].

In addition to this, simulations offer uniquely the possibility of accessing any observable of interest, since the complete information on the positions and velocities of all of the particles is available at any given time. This property of simulations allows one to determine quantities which are very difficult to access in real experiments or very hard to obtain with reasonable precision in an analytical calculation. Hence it is possible to use such simulations to test theoretical concepts and theories in a more stringent way than is feasible with real experiments. Examples of such types of simulation will be discussed below.

Despite all these advantages, reality is not quite as rosy as it might seem, since one is faced with the sad fact that computer resources are finite. Therefore it is, e.g., currently out of the question to perform a full quantum mechanical simulation for several thousand particles over a timescale of, e.g., 1 ns, and even with classical force fields and $O(10^3)$ particles it is hard to simulate times significantly longer than 100 ns, since each time step is usually only 10^{-15} s long (for atomic systems). The present state of the art is such that one can make an *ab initio* calculation for about 100 particles for a time span of 10 ps [37, 38], whereas for classical simulations one can deal with box sizes of 50–100 Å and simulate such a system for 10–100 ns [39, 40]. (Such a simulation will then usually take the equivalent of several CPU

years on a very good, dedicated workstation.) Of course, one might wonder whether it is really necessary to study systems that are larger than a few hundred particles, since it is possible to study many aspects of the glass transition even with such small systems. However, there exist situations in which large systems are necessary. For example, the *dynamics* of strong glass formers shows quite pronounced finite-size effects [40], and the same is true also for the density of states in the frequency range which is important for the so-called boson peak, a dynamic feature at low energies whose nature is currently a matter of intense debate [41, 42].

Note that, despite the above-mentioned limitations in time and system size, large-scale computer simulations cover a wave-vector and frequency range which is comparable to or even larger than, e.g., the one accessible in neutron scattering experiments, and hence they can be a valuable addition for investigating the structure and dynamics of systems on this length scale and timescale. However, it has to be emphasized that real experiments still have a crucial advantage over simulations, namely in the way in which the sample is prepared. What experimentalists do is adjust the temperature of the sample to the temperature of interest and wait for a period of the order of minutes or even weeks before they start to do the measurement. Therefore it becomes possible to probe the *equilibrium* dynamics of the system on the nanosecond scale (e.g. in the case of neutron scattering) even if the relaxation time of the system is of the order of days. In computer simulations such a procedure is not (yet) possible. The only way to equilibrate the system is to carry out a simulation at the temperature of interest for a time span that is of the order of the longest relevant relaxation time of the system and to subsequently start the run for the production. Since typical time spans of the simulation do not exceed 100 ns, it is therefore only possible to equilibrate the system at a relatively high temperature. Thus all equilibrium measurements are restricted to these temperatures as well.

In order to circumvent this problem one might be tempted to quench the system relatively rapidly to a temperature at which its relaxation time is larger than the one accessible to computer simulations, let the system relax for some time, and subsequently start to measure its properties. Such an approach is, however, quite dangerous, in that the results from such simulations will in general show aging effects. This means that quantities that should be constant (such as the average potential energy) show a small drift, and that time correlation functions will no longer be time-translation invariant. Some of these effects will be discussed in more detail in section 4.2.

We stress, however, that the above-mentioned problem with the equilibration of the sample is not a principal one. There is nothing to prevent a cleverly designed Monte Carlo algorithm from being able to also equilibrate the sample at a temperature at which, e.g., the relaxation time *for the usual Newtonian dynamics* is macroscopically large. Examples of such algorithms have already been successfully implemented for polymers, and it was found that they allow one to equilibrate the sample about 100 times faster than with the normal dynamics [43]. In recent years other methods have been proposed and tested and, although currently there is still no optimal method in sight, the progress is quite encouraging [44], and therefore it can be hoped that sooner or later this bottleneck will be removed.

Before we end this section it is appropriate to make some comments on the Hamiltonians used in simulations of supercooled liquids and glasses. Roughly speaking, simulations in this field can be divided into two types:

(i) In the first one the main goal is to use the simulation to gain an understanding of some very general question, such as to what extent MCT gives a correct description of the dynamics, the nature of the dynamical heterogeneities observed in experiments [45, 46], and the search for a diverging length scale when the temperature approaches T_g [33, 47]. Since one is interested in some universal properties of glassy systems, such simulations are usually carried out with

very simple systems, such as Lennard-Jones particles, kinetic Ising models [13], and even simpler ones (see, e.g., the backgammon model of Ritort [22]). Because of their simplicity, such models allow one to obtain results of a much higher accuracy than would be possible with more realistic and thus more complicated systems, and thus more definite answers can be given to the question of interest.

(ii) In the second type of simulation one attempts to answer some quite specific questions for a given material (or class of materials), such as that of the nature of the so-called boson peak in strong glass formers [41, 42, 48–50], that of how to identify the mechanism leading to the so-called 'mixed alkali effect' [51], and that of the nature of the distribution function of the rings in network-forming systems such as SiO_2 [38, 52–54]. For such simulations it is important to have a reliable potential at hand which is able to give a sufficiently realistic description of the quantity that one is interested in. Unfortunately it is still the exception rather than the rule for a good potential to be available for the material of interest. The reason for this is that the development of a reliable force field often involves a substantial amount of *ab initio* calculation, in order to determine the potential energy of some typical configurations, and also the subsequent fit of these data points to a classical potential energy function is often rather difficult (see, e.g., the papers of Takada *et al* [55]).

Both of these steps require a substantial amount of expertise and work, and thus have been carried out only for a few selected substances, such as silicates [56–59] and $ZnCl_2$ [60].
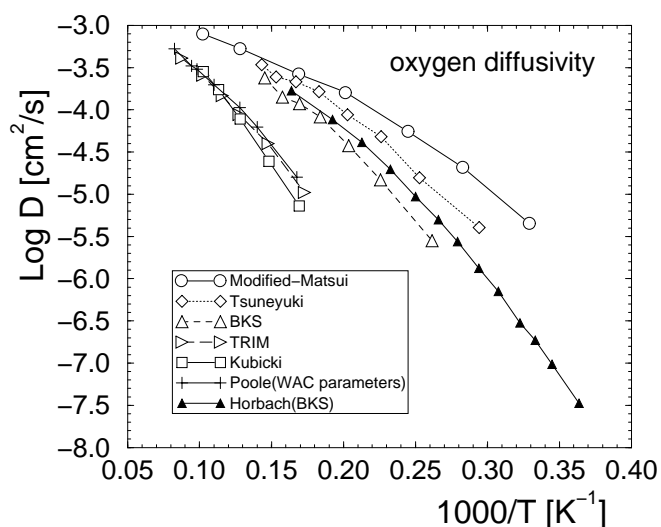

Figure 1. The temperature dependence of the oxygen diffusion constant for different models of SiO_2. See reference [61] for details. Adapted from reference [61], with permission.

It should also be noted that whether or not a potential is realistic depends on the question that one is interested in. For the case of silica, e.g., there exist many different potentials, many of which give a quite realistic representation of the *structural* properties of amorphous SiO_2, such as the structure factor [8,28,36,42,52–54,61–64]. Thus from this point of view the various potentials can be considered as essentially equivalent. If, however, *dynamical* quantities are considered, such as the diffusion constant, one finds that the various potentials lead to very different predictions. In figure 1 we reproduce data given by Hemmati and Angell in which the temperature dependence of the oxygen diffusion constant is shown for different potentials [61].

One sees that at high temperatures the values of the diffusion constants predicted by the different potentials differ only by about a factor of three. This agreement changes dramatically when the temperature is lowered, in that the different models predict diffusivities that vary over several orders of magnitude. Hence we conclude that a potential that might be appropriate to describe the structure of SiO_2 might be unsuitable for describing the dynamics of the system.

4. Some examples of computer simulations of supercooled liquids and glasses

In this section we will discuss some computer simulations of supercooled liquids and glasses. In the first part we will make a comparison between the *equilibrium* dynamics of a fragile glass former and a strong glass former in order to see what the similarities of and differences between these two types of system are. In the second part we will discuss the *non-equilibrium* (aging) dynamics of a simple glass former, i.e. the decay of the time correlation functions of the system after it has been subjected to a quench to a low temperature.

4.1. The relaxation dynamics of strong and fragile glass formers

We already mentioned at the beginning of this article that the temperature dependence of transport quantities of glass-forming liquids is not universal in that certain glass formers (called 'strong') show an Arrhenius dependence and others (called 'fragile') show strong deviations from it [15]. In this subsection we will present the results of computer simulations in which the dynamics of a simple fragile glass former and SiO_2, a prototype of a strong glass former, was investigated. By making a comparison between the two dynamics we will attempt to understand what the differences between the two types of glass former are *on the microscopic level*.

Very often, fragile glass formers are van der Waals liquids in which the interactions between the (small) molecules are relatively weak. Thus such systems can be modelled by particles with isotropic short-range interactions such as soft spheres, $V(r) \propto r^{-12}$, or the Lennard-Jones potential. Because of the simplicity of these potentials, the relaxation dynamics of such models has been studied extensively by means of computer simulations [19,65–73]. Early simulations often focused on one-component systems [74], but with the increased speed of computers it was found that such systems started to crystallize within the time span of the simulation. A simple way to avoid this problem is to use a binary mixture of particles; if the interaction parameters and the concentration of the species are chosen well, such systems stay in the (meta)stable liquid-like state for all time spans which a present state-of-the-art simulation can cover, i.e. over 100 million time steps, which corresponds to about 100 ns. A binary mixture of soft spheres, e.g., has been investigated in great detail by the group of Hansen [66], work that has been continued by Hiwatari, Odagaki, and co-workers [67], and very recently this system has been used by Parisi and co-workers to investigate aging phenomena [69, 70].

The binary system that we will discuss here consists of an 80:20 mixture of Lennard-Jones particles, with

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$$

where $\alpha, \beta \in \{A, B\}$ denotes the type of the particle (A being the majority species). 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 $\sigma_{BB} = 0.88$. For this system we will report length in units of σ_{AA}, and energy and time in units of ϵ_{AA} (setting $k_B = 1$) and $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$, respectively, where m is the mass of the particles. In the simulation we used a cubic box, of length 9.4, with periodic boundary conditions, and the total number of particles was 1000, which is large enough to

avoid finite-size effects almost completely. More details on these simulations can be found in references [72, 73].

    As already mentioned above, there exist quite a few different potentials for SiO_2 (see, e.g., the references in [54]). The one proposed by van Beest, Kramer and van Santen (BKS) [57] seems to be one of the best, in that it is able to reproduce well many of the structural and dynamical features of real silica. With this potential, the interactions ϕ_{ij} between ions i and j at a distance r apart are given by

$$\phi_{ij}(r) = \frac{q_i q_j e^2}{r} + A_{ij} \exp(-B_{ij}r) - \frac{C_{ij}}{r^6}. \tag{1}$$

Here e is the charge of an electron, and the constants A_{ij}, B_{ij}, and C_{ij} can be found in references [54, 57]. One interesting aspect of this potential is that it contains only two-body terms. This is somewhat surprising, since SiO_2 forms an open tetrahedral network and thus one might expect three-body terms to be needed as well. However, it has been shown that the BKS potential is indeed able to generate such a (disordered) tetrahedral network [54], since the competition between the different two-body forces mimics the three-body forces. As an aside, we mention that the absence of the three-body terms is of course advantageous for computer simulations, since their evaluation is usually demanding from a computational point of view. Thus the only part of the potential whose calculation is computationally intensive is the long-range Coulombic part, which is usually calculated by means of the Ewald summation [6, 75]. Since the computational effort of this method scales with $N^{3/2}$, where N is the number of particles, it is clear that performing simulations of large systems with long-range potentials is computationally much more demanding than if the potential is short ranged (in which case the computational effort thus scales like N). However, in the last few years new methods have become available in which the calculation of the long-ranged forces also (essentially) scales like N [76]. The disadvantage of these methods is that they become efficient only at relatively large N, and thus for small systems (a few hundred particles) the Ewald summation is currently the only real possibility for handling such forces. In practice this means that for a system containing of the order of 10^3 particles, the calculation of the forces on all of the particles in a system with Coulombic interactions is about one order of magnitude more time consuming than in the case of short-range interactions (e.g. the Lennard-Jones case).

    Since it has been found that the dynamics of strong glass formers shows quite large finite-size effects [40], it is necessary to use for such simulations relatively large system sizes. In the following we will discuss results of simulations in which 8016 ions have been used, which corresponds to a box size of about 48 Å. More details on the simulation can be found in references [40, 64, 77].

    Before we start the discussion of the *dynamical* behaviour of the two glass formers, we will have a brief look at the temperature dependence of the *static* structure of these systems. One possible way to do this is to investigate the partial structure factors $S_{\alpha\beta}(q)$ which are given by $\langle \rho_\alpha(q)\rho_\beta^*(q)\rangle$, where $\rho_\alpha(q)$ is the fluctuation of the density of particles of type α for wave-vector q, that is

$$\rho_\alpha(q) = \sum_{j=1}^{N_\alpha} \exp(i\boldsymbol{q} \cdot \boldsymbol{r}_j^\alpha)$$

and $\boldsymbol{r}_j^\alpha$ is the position of the jth particle of type α. In figure 2 we show the partial structure factors for the A–A and oxygen–oxygen correlations, for the Lennard-Jones and silica systems, respectively. The temperatures for the different curves range from temperatures at which the system is in its normal liquid state to temperatures at which the system is in a deeply supercooled state. From the figure it can be seen that the temperature dependence of this structural quantity
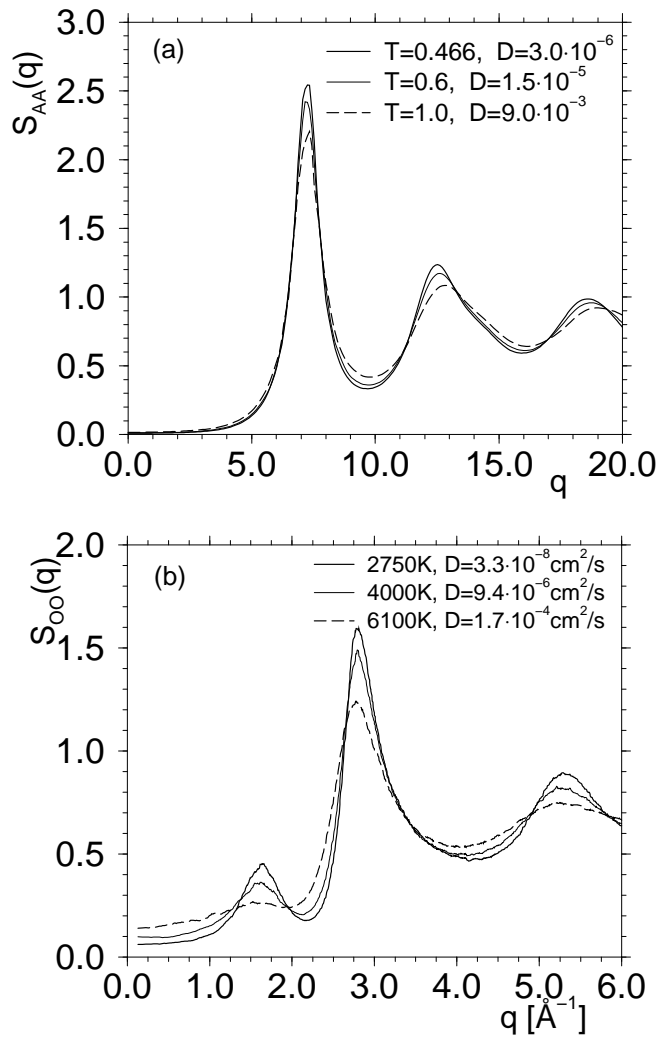
Figure 2. The wave-vector dependence of the partial static structure factor for (a) a Lennard-Jones system, a fragile glass former (A–A correlation), and (b) SiO_2, a strong glass former (oxygen–oxygen correlation). The curves correspond to different temperatures and range from the temperatures at which the system is in a normal liquid state to temperatures at which it is in a deeply supercooled liquid state. Also given are the values of the diffusion constants for the A particles (a) and the oxygen atoms (b). From references [72, 78].

is rather weak and that the main effect is that the various peaks and minima become more pronounced when the temperature is lowered. Although the static structure factors do not depend strongly on temperature, time-dependent quantities do show a strong dependence. In order to demonstrate this we have also included in the figure the diffusion constant at the different temperatures. From these figures one recognizes that in the temperature range considered, the dynamics of the system does indeed slow down quite dramatically. We will discuss this point in more detail below.

One comment on the meaning of the various peaks might be useful. In the case of a simple liquid, figure 2(a), the first peak in the structure factor corresponds to the typical inter-particle

distance. This is in contrast to the case for network-forming systems, figure 2(b), where this distance corresponds to the *second* peak in $S(q)$. The first peak in the structure factor, often called the first sharp diffraction peak [2], is related to the size of the structural units making up the network (i.e. tetrahedra in the case of SiO_2). It is interesting to see that this peak has already started to be visible at the highest temperature investigated. This means that the network is already forming at temperatures much higher than the melting temperature, which is around 2000 K. This is probably why network-forming systems are often very viscous even at very high temperatures.

It has to be emphasized that the observed (unspectacular) temperature dependence of the structure factor is not exceptional for *structural* quantities. Although several efforts have been made to find a structural quantity that shows a more pronounced temperature dependence, no clear evidence has been found so far [33, 47]. Thus the point of view that the slowing down of the dynamics of *structural* glasses is related to a second-order phase transition, and hence to the existence of a divergent length scale, is so far not supported by good evidence. (See also reference [79] on this point.)

A much more interesting dependence on temperature than the one for structural quantities is found in time-dependent correlation functions, or transport coefficients. The simplest example is $\langle r_\alpha^2(t) \rangle$, the mean squared displacement (MSD) of a tagged particle of type α:

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

where $\langle \cdot \rangle$ is the thermal average. The time dependence of the MSD for different temperatures is shown in figure 3. Let us first consider the MSD for the Lennard-Jones system. At high temperatures, top curves, the MSD shows at short times a quadratic dependence on time, $\langle r_\alpha^2(t) \rangle \propto t^2$. This behaviour can be understood immediately by realizing that for short times the particles will move ballistically, i.e. $r_i^\alpha(t) \approx r_i^\alpha(0) + \dot{r}_i^\alpha t$, and thus give rise to the observed time dependence for $\langle r_\alpha^2(t) \rangle$. For longer times the particles start to collide with their neighbours and their motion becomes diffusive. Therefore the MSD shows a linear dependence on time, as can be seen in figure 3. For low temperatures (bottom curves) the situation at short and very long times is similar to the one at high temperatures, in that the ballistic and the diffusive behaviour are observed. For intermediate times, however, the MSD shows a feature not present at high temperatures, namely a plateau. This means that there exists a time range, which at the lowest temperatures extends over several decades, in which the MSD does not increase substantially. The microscopic reason for the presence of this plateau is that the tagged particle is trapped in the cage formed by the neighbouring particles that surround it, and it takes the particle a long time to escape from this cage. Note that the particles forming this cage are of course sited in cages as well, and thus the motion of all particles is slowed down. With decreasing temperature the cages become more and more rigid, and thus the time needed to break them up increases. The earlier-mentioned MCT [11] is an attempt to describe this breaking up *in a self-consistent way* and hence to rationalize the dramatic increase of the relaxation time on a microscopic level.

In figure 3(b) we show the MSD for the oxygen atoms in the silica melt. We recognize that for this strong glass former the curves look qualitatively similar to those for the fragile glass former. The main difference is that at low temperatures the MSD for silica shows a little bump at around 0.2 ps [64, 80]. The reason for this feature lies in the so-called boson peak, a dynamical feature whose intensity seems to be related to the fragility of the glass [10], and which will be discussed in more detail below.

Using the Einstein relation

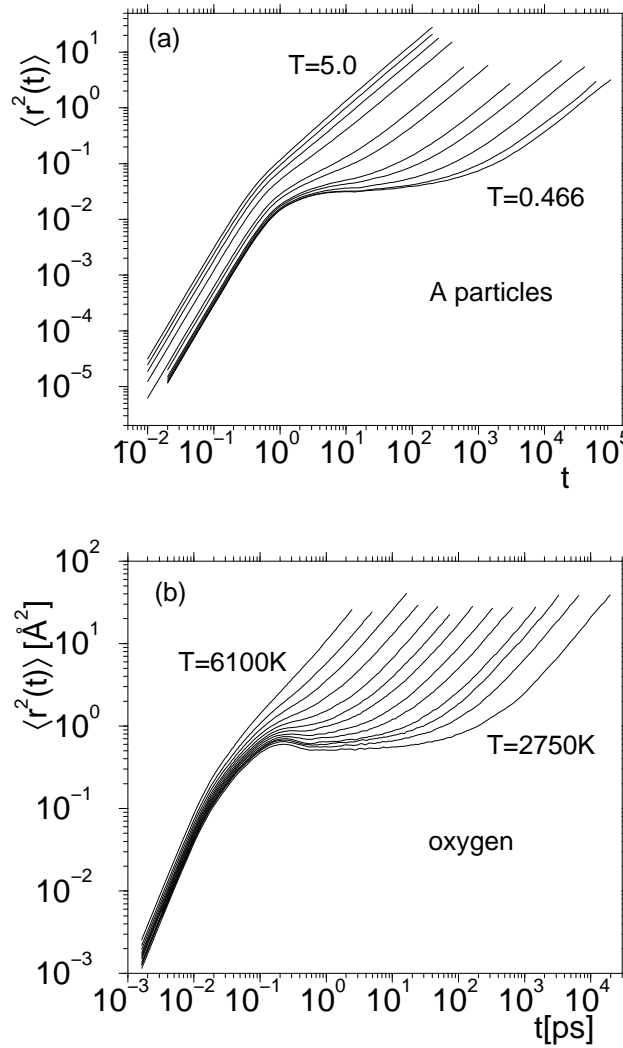$$D = \lim_{t \to \infty} \langle r^2(t) \rangle / 6t$$

Figure 3. The time dependence of the mean squared displacement for different temperatures. (a) The Lennard-Jones system. $T = 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.5, 0.475, 0.466$. (b) Silica. $T = 6100$ K, 5200 K, 4700 K, 4300 K, 4000 K, 3760 K, 3580 K, 3400 K, 3250 K, 3100 K, 3000 K, 2900 K, and 2750 K. From references [64, 73].

the diffusion constant D can be calculated from the MSD. Before we discuss the temperature dependence of D, it is useful to review a few of the predictions of MCT [11] since they will be helpful for understanding the following results. As already mentioned, this theory attempts to describe the dynamics of supercooled liquids in a self-consistent way. Most of the predictions of the theory have been worked out for that version of MCT in which certain terms in the equations of the theory, the so-called hopping terms, are neglected. This special case is called 'ideal MCT' and it is predicted that there exists a special 'critical' temperature $T_c > 0$ in the vicinity of which the dynamics shows an anomalous temperature dependence, in that the relaxation times τ, or the inverses of the diffusion constants, show a power-law divergence, $\tau \propto D^{-1} \propto (T - T_c)^{-\gamma}$. In this ideal case the system does not relax any longer if the

temperature is below T_c. If the above-mentioned hopping terms are taken into account, the divergence does not really take place. If these terms are weak, the relaxation times will show the above-mentioned power law, but slightly above T_c they will change over to showing an Arrhenius law [81]. Empirically it is found that fragile (and not so fragile) glass formers can be described well by the idealized MCT [11], whereas not too much is known about strong glass formers.
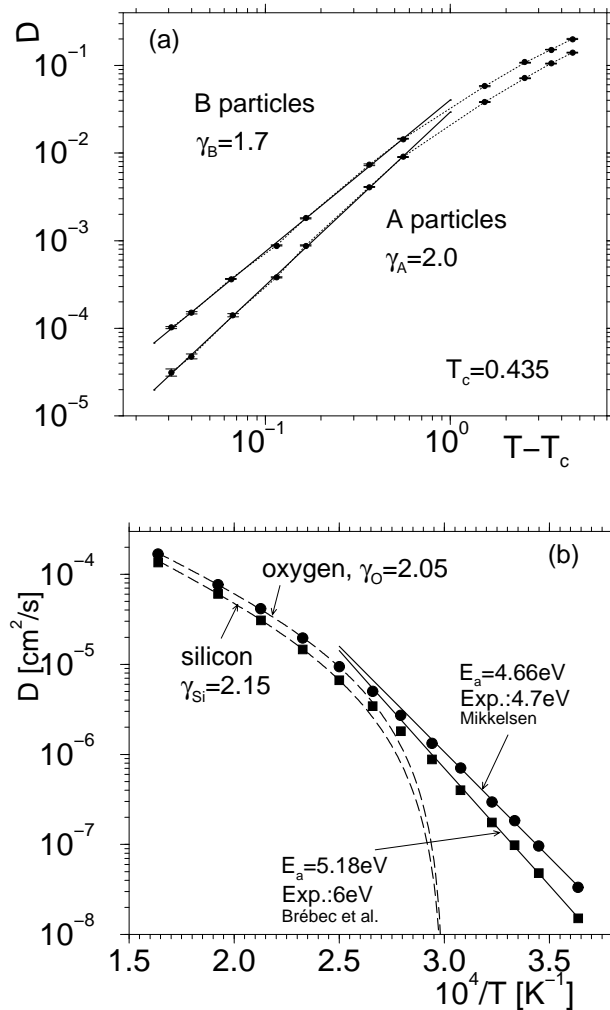

Figure 4. The temperature dependence of the diffusion constants. (a) The Lennard-Jones system. The solid lines are fits with a power law of the form $D \propto (T - T_c)^\gamma$. (b) Silica. The solid lines are fits with an Arrhenius law with the stated activation energies. The experimental values are from references [82]. The dashed curves represent power laws with $T_c = 3330$ K. From references [64, 72].

We now discuss the temperature dependence of the diffusion constants, which are shown in figure 4. Note that we use two different types of plot to present the data for the Lennard-Jones and the silica system. For the former system, a fragile glass former, we have fitted the low-temperature data with a power law in order to check whether the above-mentioned

temperature dependence predicted by MCT gives a good fit to the diffusion constant. Using T_c as a fit parameter we find that this is indeed the case (see figure 4(a)). The critical temperature T_c is the same for the A and B particles, in agreement with the prediction of MCT. According to the theory, the value of the exponent γ should also be independent of the particle species, and we find that this is reasonably well fulfilled in that for our system the two values agree to within 15% (see the figure).

We also mention that such power laws have also been found in other simulations of simple liquids [25, 66, 71], polymeric systems [26], a simple molecular liquid [27], and water [83]. The result on water is of particular interest, since H_2O is a network-forming liquid, and is thus structurally very similar to silica, the system that we will discuss next.

For silica, the temperature dependence of D is more complicated than that of fragile glass formers. Since this is a strong glass former, we expect that at low temperatures an Arrhenius behaviour will be found, and thus it is reasonable to plot the data versus $1/T$, which is done in figure 4(b). From the figure we see that at low temperatures the expected Arrhenius law is indeed observed and that the activation energies are close to the ones found in experiments [82] (see the figure). Thus we have evidence that our model for silica is quite realistic not only as regards static quantities [54, 77] but also as regards dynamical ones, at least at low temperatures.

At higher temperatures, strong deviations from the Arrhenius law are observed, in that the temperature dependence is weaker than the one expected from the activated dynamics at low T. In this temperature range the curves can be fitted well with a power law, as predicted by MCT, with a critical temperature which is independent of the species and has a value of about 3330 K (see the figure). (We also mention that the given values of γ are compatible with that from the MCT analysis of the β-relaxation regime.) Thus from the temperature dependence of the diffusion constants we have evidence that the *strong* glass former SiO_2 also shows at high enough temperatures the non-Arrhenius dependence observed for fragile glass formers. This result is in agreement with findings of Rössler and Sokolov, and Hess *et al* [84]. By analysing experimental viscosity data, these authors arrived at the conclusion that for all glass formers there exists a temperature range in which the temperature dependence of the transport coefficients is non-Arrhenius. In particular they found that for silica the value of T_c is around 3200 K, in excellent agreement with our result. Hence we conclude that the main difference between strong and fragile glass formers is that in the former the hopping processes that destroy the dynamical singularity predicted by the ideal version of MCT are so strong that the signature of this singularity, namely the power laws, accounts only for a relatively small range of the diffusion constant (or other transport quantities) before the hopping processes take over and lead to an activated dynamics. In contrast to this is the case for the fragile systems, for which the above-mentioned power law can be observed over several decades of the diffusion constant.

This point of view is also corroborated by the analysis of the self-part of the van Hove correlation function $G_s(r, t)$ [21]. This function, or rather $4\pi r^2 G_s(r, t)$, gives the probability that a particle has moved a distance r in time t. It is found that for fragile glass formers, such as the present Lennard-Jones system, this function decreases monotonically as a function of r [73], whereas for silica at intermediate and low temperatures the distribution function for the oxygen atoms shows a secondary peak at a value of r which corresponds to the typical oxygen–oxygen distance (no secondary peak is found for the silicon atoms) [77, 78]. From the existence of such a secondary peak, it has been concluded [66, 71] that the transport mechanism is not the flow-like motion described by MCT but more a jump-like motion that is activated. This point of view is thus in agreement with the one put forward above concerning the motion of the atoms in silica.

Experimentally it is not possible to measure, *for atomic systems*, time and space correlation functions like $G_s(r, t)$. However, in neutron time-of-flight measurements it is possible to study its space Fourier transform, the incoherent intermediate scattering function $F_s(q, t)$ [21]:

$$F_s(q, t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \langle \exp(i\boldsymbol{q} \cdot [\boldsymbol{r}_j^\alpha(t) - \boldsymbol{r}_j^\alpha(0)]) \rangle \qquad (3)$$

and in neutron and light scattering experiments one has access to its space and time Fourier transform, the dynamical structure factor $S(q, \omega)$. Therefore it is interesting to calculate these quantities from the simulations as well. (We note, however, that an *accurate* calculation of $S(q, \omega)$ from a simulation is rather difficult, since calculating the time Fourier transform of a correlation function that extends over 6–8 decades in time is not a simple task. Therefore results are usually presented in the time domain.)

In figure 5 we show the time dependence of the intermediate-scattering function for different temperatures. Let us first discuss the relaxation dynamics for the fragile glass former; see figure 5(a). The wave-vector q corresponds to the location of the first maximum in the structure factor (see figure 2(a)), but we have found that for the other values of q a qualitatively similar time and temperature dependence is found [72]. Following the ballistic motion of the particles at short times, giving rise to a quadratic dependence of $F_s(q, t)$ on time, the correlator shows at high temperatures a crossover to an exponential decay. For low temperatures we find a different relaxation behaviour in that, after the microscopic regime, the correlation functions show a plateau, the length of which increases rapidly with decreasing temperatures. The reason for the existence of this plateau is the same as the one that we gave in the discussion of the MSD in figure 3, namely the cage effect, i.e. the temporary trapping of the particles by their neighbours. It is customary to call the time window in which the correlator is close to the plateau the 'β-relaxation regime' and the window in which the correlator falls below the plateau the 'α-relaxation regime'.

From the figure we also recognize that at low temperatures the shape of the curves does not, in the α-relaxation regime, depend on temperature, an observation that we will discuss in more detail below. Thus the whole increase of the relaxation times is due to the dynamics in the β-relaxation regime, and hence it is this regime which has to be understood from a theoretical point of view in order to give a correct description of the relaxation dynamics, and hence the glass transition.

For the strong glass former the time dependence of the correlation functions is qualitatively similar to that for the fragile glass former. In figure 5(b) we show $F_s(q, t)$ for the oxygen atoms for a wave-vector at the location of the first sharp diffraction peak. The main, readily observable, difference between the relaxation behaviours of the fragile and the strong glass formers is that at low temperatures the latter shows a dip at around 0.2 ps, i.e. shortly after the microscopic regime and before the correlator shows the plateau. The time at which this dip occurs corresponds to about 1.5 THz, a frequency at which silica shows a pronounced enhancement of the density of states over the value expected from a Debye law [41]. Therefore this feature is called the 'boson peak' ('boson' because its temperature dependence is given by the Bose factor). Note that this feature is already observable at $T = 3580$ K, and thus at temperatures far above the (experimental) glass transition temperature of silica, which is 1450 K. (We also mention that in references [77, 78] evidence is given that the glass transition temperature of the BKS model is very close to this experimental value, thus giving further support for the reliability of this potential.) The nature of the excitations leading to the boson peak is still a matter of debate [41, 42, 49] and we do not enter that discussion here. (The issue is that of whether the peak is due to localized modes or due to a strong scattering of
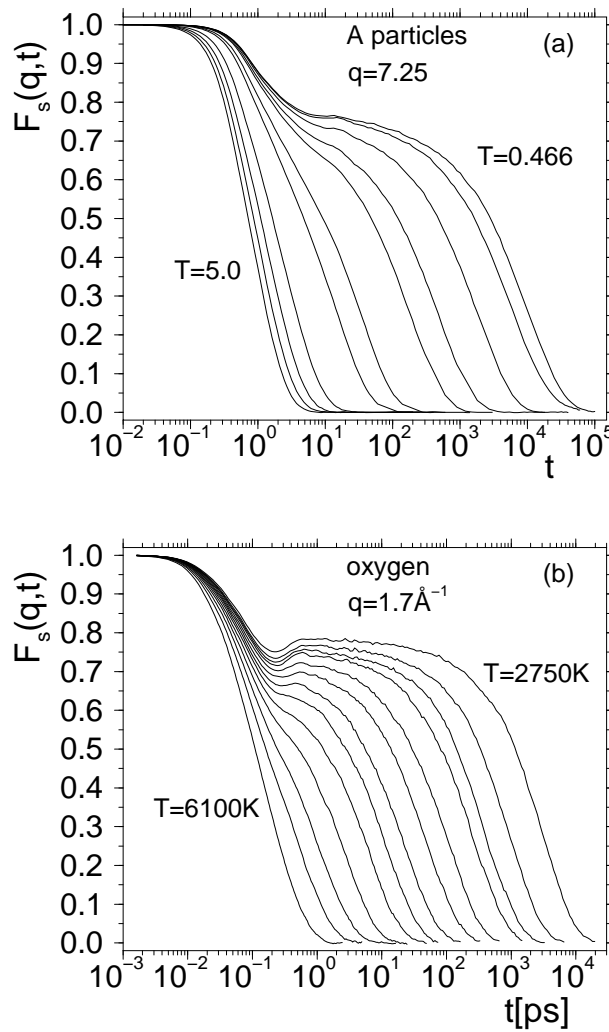
Figure 5. The time dependence of the incoherent intermediate-scattering function for different temperatures (see figure 3). (a) The Lennard-Jones system. (b) Silica. From references [64, 72].

sound waves.) We mention, however, that it was found from computer simulations of systems with different sizes that the depth of the dip in $F_s(q, t)$ depends strongly on the size of the system and that these finite-size effects become more severe with decreasing temperature [40]. Thus it can be concluded that the excitations that give rise to this feature involve cooperative motion that extends at least over several nanometres and that, in order to finally find the answer concerning the nature of the peak, large systems ($O(10^4)$ ions) have to be analysed so that the finite-size effects mentioned can be avoided.

A further difference between the relaxation behaviours of strong and fragile glass formers is concerned with the temperature dependence of the height of the plateau in time correlation functions. This effect can be studied best if one plots the correlation functions versus the rescaled time $t/\tau(T)$, where $\tau(T)$ is the α-relaxation time at temperature T. This time can, e.g., be defined as the time that it takes a correlation function to decay to e^{-1} of its initial value.
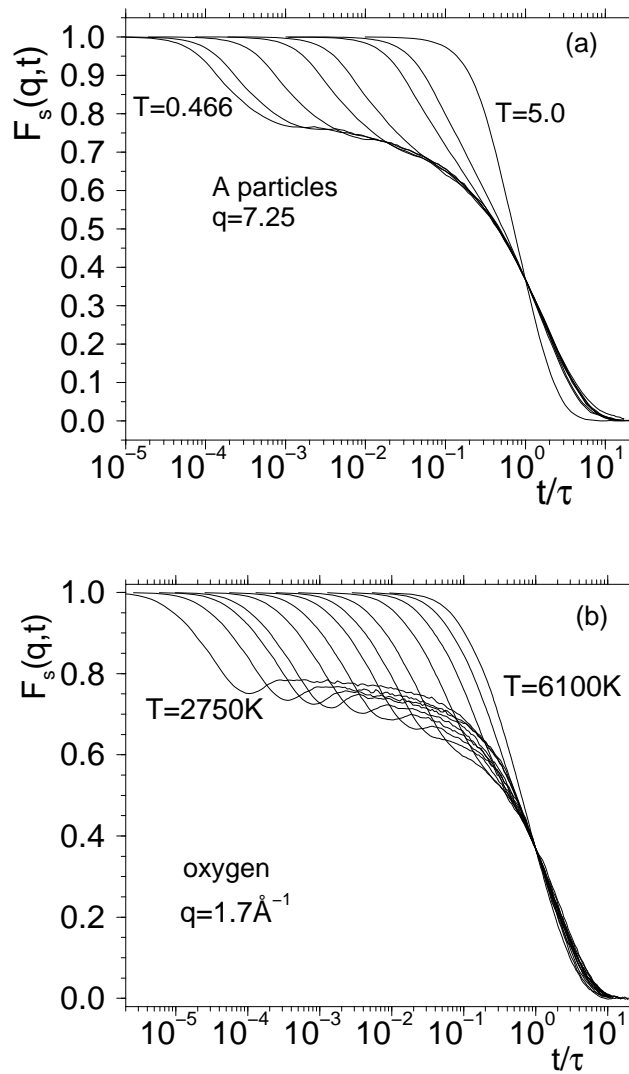
Figure 6. The incoherent intermediate-scattering function versus rescaled time for different temperatures (see figure 3). (a) The Lennard-Jones system. The curves for $T = 4.0$, 3.0, and 2.0 are not shown. (b) Silica. From references [64, 72].

(Another possibility would be to define it as the area under the correlator.) In figure 6 we show the so-obtained figures for the same correlators as are shown in figure 5. For the fragile glass former we find that, at low temperatures, this scaling leads to a master curve which extends throughout the whole α-regime, i.e. that part of the relaxation in which the correlators fall below the plateau. Such a master curve has been found also in other simulations [25–27,66,71] and in experiments [12], and its existence is one of the important predictions of MCT. The existence of this master curve is by no means trivial, as can be recognized from the corresponding plot for silica (figure 6(b)) since for this system the scaled curve, in the vicinity of the plateau, does not fall onto a master curve at all. A detailed analysis of the individual curves shows,

however, that, in the β-relaxation regime, the *shape* of the curves is indeed independent of temperature [77, 78]. Thus the only reason for them not falling onto a master curve is the presence of the boson peak at short times, which leads to a temperature-dependent height of the plateau. Also, in experiments it has been found that for strong glass formers the boson peak dominates the time dependence of the correlation function in the time range where the correlators approach the plateau [10]. Most of these findings stem, however, from experiments in which the system is probed in the frequency domain (such as by means of light scattering). Therefore such experiments, if done at frequencies $\omega > 0$, will in general not 'notice' whether or not the height of the plateau depends on temperature, since such a dependency will affect only the intensity of the signal at frequency zero. Thus the results from the computer simulation do indeed give new insight into the dynamics of strong glass formers.

Above, we have shown that for the case of silica the power law predicted by MCT for the temperature dependence of D can be observed only for a relatively small range of the diffusion constant. From figure 6(b) one sees that, due to the strong influence of the boson peak in the β-relaxation regime, the predicted master curve is also not observed. Therefore one *might* be tempted to argue that MCT is not a very useful description of the dynamics of SiO_2. This point of view is, however, far too pessimistic, since there are predictions of the theory which are also valid in the presence of the above-mentioned hopping processes, such as the so-called factorization property, which states that in the β-relaxation regime any time correlation function $\Phi(t)$ can be written as $\Phi(t) = f + hG(t)$, where $G(t)$ is a universal function of the system, and f and h will depend on the correlation function Φ. It has been shown [77, 78] that for the case of silica this factorization property holds very well, thus showing that MCT is able to make relevant (and correct) predictions on the dynamics for this (strong) type of glass former as well.

Having now some understanding of the temperature dependence of the relaxation dynamics of the Lennard-Jones and the silica system, we can compare it with that of other glass formers. Sciortino *et al* have carried out extensive simulations of the dynamics of supercooled water [83], a system which shares many structural and thermodynamical properties with silica [3, 30, 62, 85]. These simulations have shown that in the temperature range accessible to equilibrium simulations, the diffusion constant shows a power-law dependence [83], a result that is supported also by experiments [3, 86]. Thus, although the system is *structurally* much more similar to the strong glass former silica, it behaves *dynamically* like a fragile glass former. From our findings for silica we therefore conclude that the strong hopping processes found in silica are less pronounced in water than in silica (which might, however, also have to do with the fact that the water simulations have been done with H_2O molecules that could not dissociate).

For the early β-relaxation regime it is found [83] that water also shows a small dip, like the one that we showed to be present for silica (see figure 6(b)). However, contrary to the case for silica, this dip does not destroy the master curve in the late β-relaxation regime when the correlators are plotted versus $t/\tau(T)$. Thus the dynamics of water seems to behave in certain respects like that of a fragile glass former and in other respects like that of a strong one. This duality is most probably due to the network structure, since the simple atomic and molecular liquids, that do not have the tendency to form a network, have been found to show essentially the same dynamics as the Lennard-Jones system discussed here [25, 27, 66, 71, 87]. Also the dynamics of polymeric glass formers is in many aspects quite similar to that of simple liquids [26]. However, because of the length of the molecules, these systems also show interesting dynamic effects which are not present for simple liquids, such as the motion of side chains or reptative movements. For a more thorough discussion of these issues, we refer the reader to the review articles by Clarke [88] and Paul and Baschnagel [89].

The results presented so far are mainly useful for understanding the slowing down of the relaxation dynamics on a *qualitative* level. However, it is also possible to use computer simulations to study this relaxation dynamics on a *quantitative* level and thus to test predictions of theories that attempt to describe this dynamics. In the following we will therefore briefly describe a few simulations which have been carried out to test the validity of such theories.

As already mentioned in section 2, two very prominent theories are the ones of Gibbs and DiMarzio [20], which is very popular in the community of polymer scientists, and the so-called mode-coupling theory, which seems to be applicable for a very large variety of glass formers [11]. The basic ideas of these two theories are very different.

In the Gibbs–DiMarzio approach one starts from polymers which are placed on a lattice. By counting the number of ways in which the polymers of the melt can be placed on the lattice, Gibbs and DiMarzio found that there exists a critical packing fraction above which this configurational entropy goes to zero in a continuous way. From this they concluded that a second-order phase transition exists at this point, which is accompanied by the usual critical slowing down of the dynamics. This slowing down then gives rise to the glass transition. It has been found that this theory is able, e.g., to rationalize the dependence of the glass transition temperature on the length of the polymers, on the concentration of plasticizer, and other relevant quantities [90]. It was therefore quite surprising when a few years ago a simulation carried out by Wolfgardt *et al* showed that the observed slowing down of the relaxation dynamics of a dense polymer melt is *not* due to the configurational entropy of the system becoming zero [91]. This can be seen in figure 7 in which the entropy is plotted versus the inverse temperature. The open symbols correspond to the entropy as given by the (approximate) expression proposed by Gibbs and DiMarzio, and one sees that this prediction gives a zero value of the entropy at a finite temperature. (It has to be emphasized that the quantities entering the Gibbs–DiMarzio expression have been calculated from the simulation as well, and thus no approximation on that level is made.) The filled symbols are the real values of the entropy of the system which have been measured by thermodynamic integration. From the figure it becomes clear that this real entropy does not go to zero in the temperature range in which the Gibbs–DiMarzio
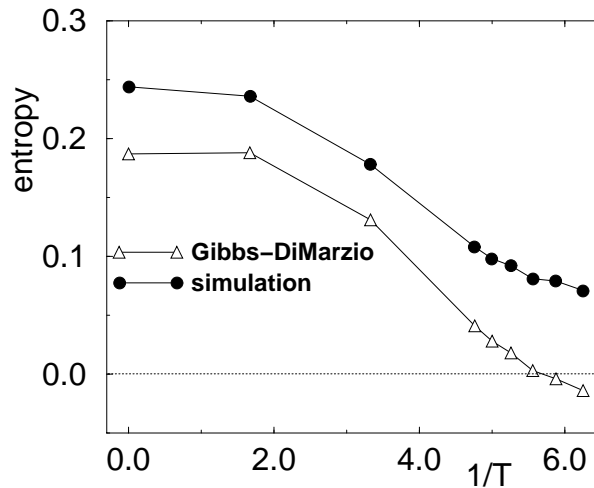

Figure 7. The temperature dependence of the configurational entropy for a polymer model as determined from a Monte Carlo simulation (filled symbols) and from the prediction of the theory given by Gibbs and DiMarzio (open symbols). Adapted from reference [91].

expression becomes zero, but that it does show a noticeable decrease in this temperature range. Thus one has to conclude that the success of the Gibbs–DiMarzio theory probably relies on the fact that the real entropy decreases significantly in the vicinity of the critical temperature, that the theory gives a quite realistic description of this decrease *on the qualitative level*, and that most experiments measure only quantities which are related to the various *derivatives* of the entropy.

The second theory that we will discuss here to some extent, the mode-coupling theory, has a very different explanation for the slowing down of the system upon cooling. From the theory of the dynamics of simple liquids in the vicinity of the triple point, it is known that the equations of motion for density correlation functions have non-linear terms which are needed to describe back-flow effects and cage effects [92], and the MCT constitutes such a set of equations of motion. It is found that with decreasing temperature the non-linear terms become stronger and will lead to a dynamical feedback effect that slows down the relaxation of the density correlators. Within a certain approximation to these equations, leading to what is known as the 'ideal MCT', this feedback mechanism becomes so strong that at a certain temperature T_c the correlation functions do not decay to zero any longer, i.e. the system has undergone a glass transition. Using this temperature T_c as a reference temperature, the theory makes detailed predictions regarding the time and temperature dependence of correlation functions, such as the intermediate-scattering function discussed above.

One of the important aspects of the theory is that the equations of motion for the density correlators depend only on *static* quantities, such as the structure factor. Since such quantities can be obtained quite easily with high precision from experiments or simulations, it is thus possible to measure the static quantities, solve the MCT equations, and compare the so-obtained theoretical curves for the time-dependent correlation functions with the one measured in an experiment or in a computer simulation. Therefore very stringent tests of the theory become possible on a qualitative as well as *quantitative* level.

The outcome of such a test has recently been reported by Nauroth and Kob [93]. In that work the MCT equations for the binary Lennard-Jones system discussed above have been solved numerically and their solutions at long times compared with the results from simulations. Among the quantities investigated were the wave-vector dependence of the height of the plateau in the intermediate-scattering function (see figure 5) at the critical temperature T_c, a quantity which is also called the Edwards–Anderson, or non-ergodicity parameter $f_c(q)$.

In figure 8 we show $f_c(q)$ as predicted by MCT (solid curves) and that from the computer simulation (open symbols). The Gaussian-shaped curve shows the non-ergodicity parameter for the incoherent intermediate-scattering function F_s of the A particles (equation (3)) and the oscillatory curves are for the coherent intermediate-scattering function for the A–A correlation [21]. We emphasize that for the calculation of the theoretical curves no fit parameter of any kind was used. The only input was the temperature dependence of the partial structure factors, which were determined from the simulation. From the figure we recognize that the theory gives an excellent description of the wave-vector dependence of f_c and we thus conclude that the theory is indeed able to make precise *quantitative* predictions on the dynamics of supercooled simple liquids.

Also included in the figure are the results of a computer simulation of the above-mentioned binary Lennard-Jones system, but instead of the Newtonian dynamics used in reference [72] a Brownian-like (stochastic) dynamics was used [94]. In this type of dynamics the equations of motion of the particles are given by

$$m\ddot{\boldsymbol{r}}_j + \sum_{i \neq j} \frac{\partial V(|\boldsymbol{r}_i - \boldsymbol{r}_j|)}{\partial \boldsymbol{r}_j} + \zeta \dot{\boldsymbol{r}}_j + \eta_j(t) = 0 \tag{4}$$
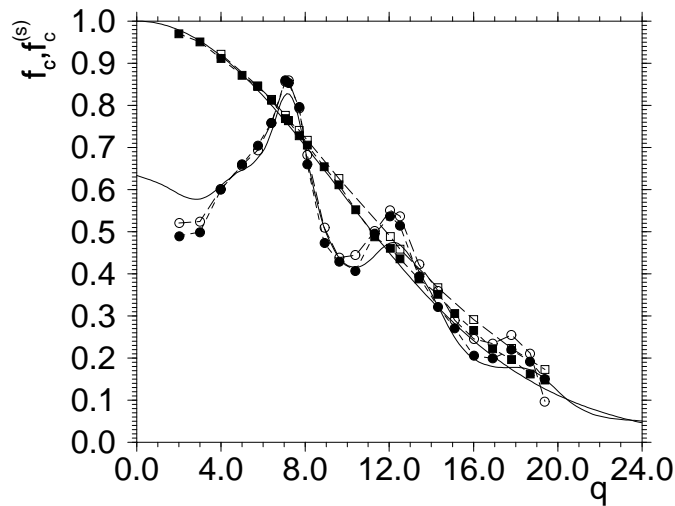
Figure 8. The wave-vector dependence of the non-ergodicity parameter as predicted from MCT (solid curves), as measured in a Lennard-Jones system with Newtonian dynamics (open symbols) and a stochastic dynamics (filled symbols). The Gaussian-shaped curves are for the incoherent intermediate-scattering function and the oscillatory curves are for the coherent intermediate-scattering function. From reference [94].

where ζ is a friction constant whose value is related to the amplitude of the white noise $\eta_j(t)$ by the fluctuation-dissipation theorem, that is

$$\langle \eta_j(t)\eta_i(t') \rangle = 6k_B T \delta(t - t')\delta_{ji}.$$

There are two reasons for studying a system with such a stochastic dynamics. Firstly the system with these stochastic forces will probably have a dynamics which is quite similar to that of a colloidal particle in a suspension, a model system for which beautiful light scattering experiments have been performed to study the glass transition [12]. Thus it is interesting to see whether the relaxation dynamics of the Lennard-Jones system is indeed very similar to the one found in these experiments. The second reason is related to a prediction of MCT which states that at long times the relaxation dynamics is independent of the microscopic dynamics. Thus we can compare the relaxation behaviour of the system with the stochastic dynamics with that of the system with the Newtonian dynamics, and see in what respects the two differ. Work in this direction has already been done by Löwen *et al* [95]. These authors made a simulation of a supercooled polydisperse mixture of particles interacting with a Yukawa potential, and compared the relaxation dynamics of this system with a Newtonian dynamics to that of a system with a Brownian dynamics. It was found that in the β-relaxation regime the dynamics depends on the microscopic dynamics, but that the α-relaxation was independent of it. Qualitatively similar results have been found by Gleim *et al* in the above-mentioned simulation of the Lennard-Jones system [94,96]. In that work it was shown that at low temperatures the entire relaxation dynamics is independent of the microscopic dynamics, if one leaves aside the relaxation at very short (microscopic) times. An example illustrating this finding is shown in figure 8, were we have also included the wave-vector dependence of the non-ergodicity parameter for the system with the stochastic dynamics (filled symbols). We see that this q-dependence is essentially independent of the microscopic dynamics, thus confirming this prediction of the theory. Furthermore, we also recognize that for essentially all wave-vectors the curves for the stochastic dynamics agree even better with the theoretical

ones than the curves for the Newtonian dynamics do. The reason for this might be that MCT assumes that the timescale of the β-relaxation, at which the height of the plateau is measured, is separated well from that of the microscopic relaxation. Since in the stochastic dynamics the phonons are strongly damped, it can be expected that *effectively* this separation is larger in the case of the stochastic dynamics than for the case of the Newtonian dynamics, where no damping is present, and that therefore the assumption of the theory is better fulfilled.

4.2. Dynamics below the glass transition temperature

In the previous subsection we have discussed the equilibrium relaxation dynamics of glass-forming liquids in their supercooled state, i.e. at temperatures above the glass transition temperature T_g. Since we have seen that with decreasing temperature the relaxation time τ increases quickly, we expect that there will exist a temperature T_g at which τ will exceed the timescale of the experiment or simulation, and hence it will no longer be possible to equilibrate the system. One might guess that at temperatures below T_g the system is essentially frozen, i.e. that its dynamics is similar to the vibrational dynamics of a solid. To a certain extent this view is certainly correct, and solid-state concepts, like the density of states, have successfully been applied to describe the dynamics of disordered systems and to compute their specific heat [97]. However, as we will show in this section, even at low temperatures the dynamics of disordered systems is not purely of vibrational type but has also a very interesting relaxational component. This slow relaxation is known as 'aging' and leads to a slow time dependence of various material properties, such as brittleness and density. The importance of such aging phenomena has been realized for quite a long time [98] (and they have been described by means of phenomenological theories) but it is only in recent years that sound theoretical concepts have been developed in order to describe this type of dynamics [99–102]. Apart from extensive investigations on polymeric systems [98], aging phenomena have so far mainly been investigated in spin glasses by means of experiments and computer simulations [16, 99, 103, 104]. Only very recently have experiments and computer simulations of structural glasses and other disordered systems been carried out in order to investigate these phenomena [70, 105–111] so that the validity of the various theoretical approaches can be tested. The results of these investigations do not yet allow one to decide which one of the theoretical pictures proposed ('droplet model', 'trap model', mean-field picture) [99–102, 106] is appropriate for describing the aging dynamics of structural glasses, but it can be expected that further studies will ultimately rule out certain scenarios. Therefore the goal of the following presentation of the results of such investigations is not to advocate any particular theory but rather to familiarize the reader with the effects occurring and to show how computer simulations might help one to decide which theoretical picture is appropriate for describing this aging dynamics.

In order to study aging effects it is of course necessary to first drive the system out of equilibrium. In structural glasses this can be done, e.g., by decreasing the temperature below the glass transition temperature or by compressing the system beyond a 'critical' density. If the out-of-equilibrium situation is generated by a temperature jump, one proceeds as follows. The system is first equilibrated at an initial temperature $T_i > T_g$. At time $t = 0$ the system is quenched to a temperature T_f which is significantly lower than the glass transition temperature T_g, where T_g is given by the timescale of the experiment. After the quench the system is allowed to evolve for a waiting time t_w, after which the measurements start. The relaxation of the system is now studied as a function of t_w and τ, the time elapsed since the start of the measurement, i.e. since $t = t_w$. In a recent computer simulation, Kob and Barrat studied the relaxation dynamics of the binary Lennard-Jones system discussed above after such a quench
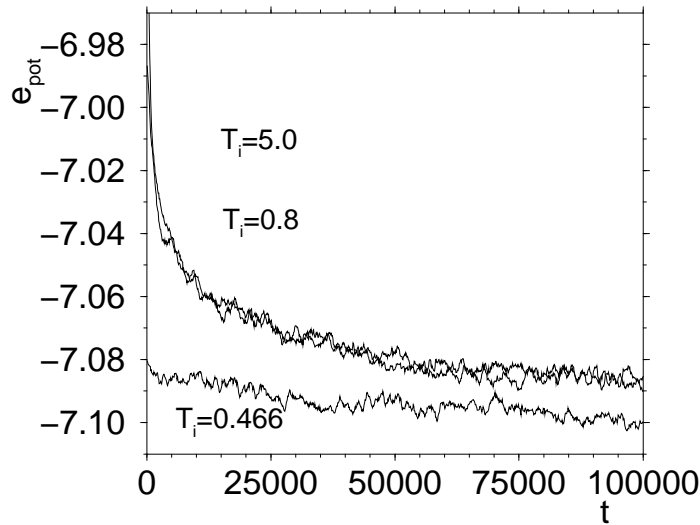
Figure 9. The time dependence of the potential energy of a Lennard-Jones system which at time zero has been quenched from an initial temperature T_i to a final temperature $T_f = 0.4$. Adapted from reference [108].

(reference [108]). In figure 9 we show the time dependence of e_{pot}, the potential energy of the system, after such a quench to $T_f = 0.4$ for three different initial temperatures $T_i = 5.0, 0.8$, and 0.466. Note that the glass transition temperature of the system for very long simulations ($O(10^8)$ time steps) is around $T_c = 0.435$ [72]. One recognizes that, after a relatively fast decay, the potential energy for the two larger values of T_i is almost constant and also the curve for the lowest T_i depends only weakly on time. A more careful analysis of this time dependence shows that it is approximated well by a power law with a small exponent around 0.14, or by a logarithmic time dependence. Since this dependence is so weak, one might erroneously conclude that at the end of the run the system has equilibrated, or is at least quite close to equilibrium. We know, however, that this is clearly not the case, since we are at a temperature at which the relaxation time of the system exceeds by several orders of magnitude the timescale of the simulation. Hence this should be taken as a warning against using a one-time quantity as a probe of whether or not the system has been equilibrated. (By 'one-time quantity' we mean an observable which *in equilibrium* is a constant, such as the energy, pressure, and density.) Thus we conclude that the investigation of such quantities is not very well suited for studying aging phenomena, a result in agreement with simulations by Andrejew and Baschnagel of aging effects in a polymer melt (reference [110]).

Much more sensitive quantities used to study the aging dynamics are 'two-time' correlation functions, such as the generalization of the intermediate-scattering function $F_s(q, t)$ (equation (3)) to a non-equilibrium situation. We recall that by definition of equilibrium, a time correlation function depends only on *time differences*; that is,

$$F_s(q, \tau) = \frac{1}{N} \sum_{j=1}^{N} \langle \exp(i\boldsymbol{q} \cdot [\boldsymbol{r}_j(\tau) - \boldsymbol{r}_j(0)]) \rangle = \frac{1}{N} \sum_{j=1}^{N} \langle \exp(i\boldsymbol{q} \cdot [\boldsymbol{r}_j(t_w + \tau) - \boldsymbol{r}_j(t_w)]) \rangle.$$

(5)

Since the quench breaks the time-translation invariance of the system, the second equality no
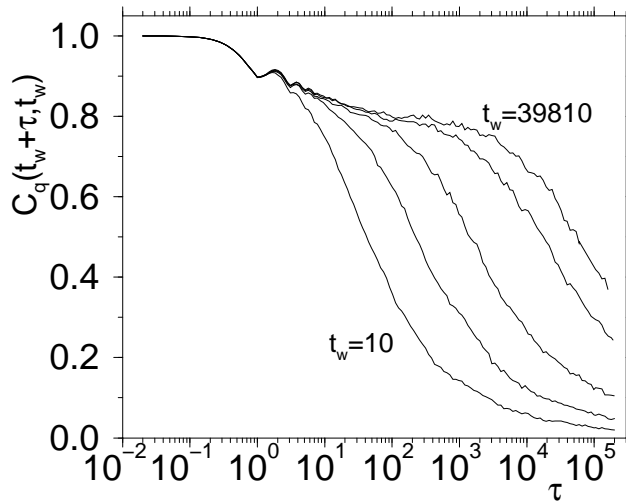
Figure 10. The time dependence of the out-of-equilibrium correlation function $C_q(t_w + \tau, t_w)$ for different waiting times t_w. From left to right: $t_w = 10$, 100, 1000, 10 000, and 39 810. The wave-vector q is 7.25, the location of the maximum in the static structure factor. Adapted from reference [108].

longer holds, and we therefore define the out-of-equilibrium time correlation function

$$C_q(t_w + \tau, t_w) = \frac{1}{N} \sum_{j=1}^{N} \langle \exp(i\boldsymbol{q} \cdot [\boldsymbol{r}_j(t_w + \tau) - \boldsymbol{r}_j(t_w)]) \rangle. \tag{6}$$

Here $\langle \cdot \rangle$ stands for the average over the temperature *before* the quench. The time dependence of $C_q(t_w + \tau, t_w)$ for different waiting times is shown in figure 10. We see that this two-time correlation function shows a very strong dependence on the waiting time and is therefore well suited for studying the aging dynamics. For small t_w, the function decays very quickly, since the typical configuration of the particles at T_f is very different from the one at T_i. Therefore the system is subject to a large driving force which will move it towards a part of phase space which is more typical for the temperature T_f, and thus the system will quickly decorrelate from the initial configuration. If the waiting time is increased, the driving force becomes smaller, and at short and intermediate times τ the system will explore only that part of phase space which corresponds to the vibrational motion of the particles in their cages. This is why the correlation functions show a plateau at intermediate times and look qualitatively quite similar to the ones in equilibrium (cf. figure 5(a)). Only for larger times τ does the correlation function decay to zero, and the time at which this final decay is observed increases with t_w. Although the off-equilibrium relaxation curves $C_q(t_w + \tau, t_w)$ for large t_w look qualitatively similar to the ones in equilibrium (i.e. to $F_s(q, t)$), a detailed analysis shows that there are important differences. For example, it is well known that at long times the equilibrium relaxation curves of glass-forming liquids can be fitted very well by a Kohlrausch–Williams–Watts function, $A \exp(-(t/\tau_{KWW})^\beta)$, and this is also the case for the present Lennard-Jones system [72]. For the out-of-equilibrium function it is, however, found that the relaxation at long times is given by a power law with an exponent around 0.4 (reference [111]), a result which is in qualitative agreement with results of simulations of spin glasses [16, 104]. Hence we conclude that, despite the apparent similarity of the curves for equilibrium and out-of-equilibrium relaxation,

the two types of function differ significantly. Therefore it is not appropriate to use the latter ones as an approximation for the former ones, as is sometimes done when time correlation functions for temperatures above and below T_g (as determined from the simulation) are mixed together in the analysis of the data.

In the discussion of figure 9, we concluded that a one-time quantity is not a good indicator of whether or not the system has reached equilibrium. Often it is argued that the decay of a time correlation function, or seeing a diffusive (i.e. linear) time dependence of the mean squared displacement within the time span of the simulation, is a sufficient condition for having reached equilibrium. From figure 10 one recognizes, however, that this is not the case at all, since the correlation functions also decay in the non-equilibrium situation, a result which was also demonstrated nicely by Baschnagel (reference [112]), and in a recent simulation of a soft-sphere system Parisi demonstrated that a linear dependence of the MSD does not imply at all that one has reached equilibrium [70].

One of the interesting results of the theories of aging concerns the violation of the fluctuation-dissipation theorem (FDT) [99, 101], which in equilibrium relates $R_A(t)$, the response of an observable A to its conjugate field, to the time autocorrelation function $C_A(t) = \langle A(t)A(0)\rangle$, i.e. $R_A(t) = -(k_B T)^{-1}\, \partial C_A(t)/\partial t$. For the out-of-equilibrium case this relation is no longer valid, and it is generalized to

$$R_A(t', t) = \frac{1}{k_B T} X_A(t', t) \frac{\partial C_A(t', t)}{\partial t} \tag{7}$$

where $t' \geqslant t$, and the quantity $X_A(t', t) \leqslant 1$ is defined by this equation. From this relation it becomes clear that the quantity $T/X_A(t', t)$ can be viewed as the effective temperature for which the FTD holds (reference [113]; see also reference [101]). Note that in the field of glass science, the concept of a 'fictive' temperature was introduced long ago by Tool and Eichlin (reference [114]) but, to our knowledge, has never been based on a solid statistical mechanics foundation. In contrast to this, the definition of such a temperature via equation (7) does not have this drawback and permits one to measure this temperature in experiments or simulations. From the equation it also becomes immediately obvious that the ratio $T/X_A(t', t)$ will in general depend on time and on the observable considered.

If the observable of interest is the coherent intermediate-scattering function $C_q(t_w + \tau, t_w)$, one can measure the response $R(t_w + \tau, t_w)$ (in principle) as follows†. After the waiting time t_w, a space-dependent sinusoidal field with wave-vector q, which couples to the particle density and has an amplitude V_0, is turned on, and the resulting change in the density distribution for wave-vector q is measured. After a measuring time τ one therefore obtains the integrated response $M(t_w + \tau, t_w)$ given by

$$V_0 M(t_w + \tau, t_w) = V_0 \int_{t_w}^{t_w + \tau} R(t_w + \tau, t) \, \mathrm{d}t. \tag{8}$$

For large values of τ and t_w, the FDT-violation factor $X(t_w + \tau, t_w)$ in equation (7) is expected to become a function of $C(t_w + \tau, t_w)$ only, i.e. $X(t_w + \tau, t_w) = x(C(t_w + \tau, t_w))$, where x is a function of *one* variable [99]. From this relation and equation (8), one thus derives

$$M(C_q) = \frac{1}{k_B T} \int_{C_q}^{1} x(c) \, \mathrm{d}c \tag{9}$$

where we have used the fact that $C_q(t_w + \tau, t_w) = 1$ for $\tau = 0$. This equation thus indicates that a parametric plot of $k_B T M$ versus C_q, with time τ as a parameter, will give us information on the function $x(c)$ and hence on the FDT-violation factor $X(t_w + \tau, t_w)$.

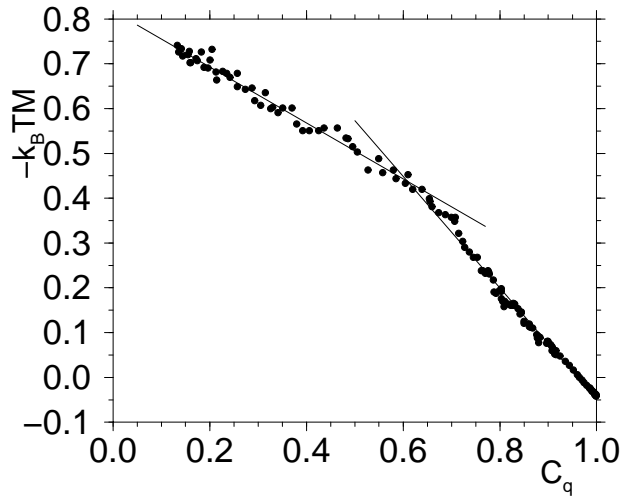† More details on this calculation can be found in reference [109].

Figure 11. A parametric plot of the integrated response M versus the two-time correlation function C_q. The two straight lines have slopes around -0.6 and -1, respectively. Adapted from reference [111].

In figure 11 we show such a parametric plot for the same correlation function as is shown in figure 10, and the corresponding integrated response M. The values of t_w and T_f are 1000 and 0.4, respectively. We see that for short times τ, corresponding to large values of C_q, the data points can be approximated well by a straight line with a slope around -1 (see the figure). This means that the FDT-violation factor X is 1, i.e. that the FDT holds and the system behaves like it does in equilibrium. However, for larger times (corresponding to smaller values of C_q) the FDT is violated, since the data points do not fall any longer on a straight line with slope -1. What is observed instead is a straight line with a slope around -0.62. This means that in this time regime, $X(t_w + \tau, t_w)$ is constant and has a value around 0.62, which corresponds to an effective temperature of $0.4/0.62 \approx 0.64$. Qualitatively similar results have been found in the seminal work of Parisi, in which the violation of the FDT has been investigated for a soft-sphere system [70]. In that simulation the observable of interest was the mean squared displacement, and it was shown that the FDT-violation factor X shows a linear dependence on the final temperature T_f of the quench, a result which has been confirmed also by Barrat and Kob (reference [109]).

Note that the fact that in the non-FDT region we find a straight line with a *finite* slope is not trivial at all, since certain theories of aging, such as that of domain growth (reference [102]), predict a straight line with slope zero and others a parabola-like dependence [99]. Hence we see that these types of measurements can indeed be used to collect evidence for or against a theoretical scenario.

5. Conclusions

In this review we have discussed some results of computer simulations of supercooled liquids. The literature on this topic is now so vast that a comprehensive review is unfortunately no longer possible and thus we have focused on only a few topics, namely on the (metastable) equilibrium dynamics above T_g for a strong and fragile glass former and on the non-equilibrium dynamics below T_g. Whereas the investigation of the former type of question is today still

dominated by real experiments, the latter seems to have been studied in much more detail by means of computer simulations, since for the moment they are better adapted for investigating such problems. We hope however that in the near future this situation will change, since such investigations allow us to learn more about the structure of the phase space of the system. (We mention that in the past, some properties of phase space have been investigated by determining the inherent structure of liquids and studying normal modes (reference [115]).) If the structure of this phase space is understood well—e.g. if we know whether or not it is organized in a hierarchical way—it might become possible to understand the connection between systems in which the disorder is quenched (such as spin glasses) and systems with self-generated disorder (e.g. structural glasses).

Other types of question in which computer simulations are probably very valuable are those regarding the investigation of the *equilibrium* dynamics of supercooled liquids in the region between the MCT temperature T_c and the experimental glass transition T_g on a microscopic level. Although for fragile glass formers such simulations are currently not quite feasible, they will be possible in a few years. Since at the moment there is no complete theory for the dynamics of liquids in this temperature range, and real experiments rarely allow one to probe the system on the microscopic level in sufficient detail, such simulations will constitute an excellent tool for gaining insight into this question and thus may possibly serve as a guide to the development of reliable theories.

Apart from these types of simulation, which are motivated mainly by the wish to have a sound theoretical understanding of glassy materials, there are of course also those simulations which are carried out to calculate properties of specific materials. For example, it is possible to predict the temperature dependence of the specific heat of silica, for temperatures above 100 K up to T_g, to within a few per cent of the experimental values [97], and the dynamic structure factor with quite high accuracy [42, 77, 78]. It can be expected that in a few years the quality of the available potentials will increase even further, and that soon potentials of somewhat more exotic materials (such as multicomponent systems) will also be determined. This will then in turn open the door to many types of simulation related more closely to materials science, and thus allow one to apply all the know-how and insight gained in the investigation of less complex models also to technologically more relevant materials.

Acknowledgments

References

[1] See, e.g., Douglas R W and Frank S 1972 *A History of Glassmaking* (Henley on Thames: Foulis)
[2] Zallen R 1983 *The Physics of Amorphous Materials* (New York: Wiley)
      Jäckle J 1986 *Rep. Prog. Phys.* **49** 171
      Uhlmann D R and Kreidl N J (ed) 1986 *Glass Science and Technology: Viscosity and Relaxation* vol 3 (Orlando, FL: Academic)

Zarzycki J (ed) 1991 *Materials Science and Technology* vol 9 (Weinheim: VCH)

Feltz A 1993 *Amorphous Inorganic Materials and Glasses* (Weinheim: VCH)

Mohanty U 1995 *Adv. Chem. Phys.* **89** 89

Ngai K L (ed) 1998 *Proc. 3rd Int. Discussion Mtg on Relaxation in Complex Systems; J. Non-Cryst. Solids* **235–238**

[3] Debenedetti P G 1997 *Metastable Liquids* (Princeton, NJ: Princeton University Press)

[4] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801

[5] Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A H and Teller E 1953 *J. Chem. Phys.* **21** 1087

Alder B J and Wainwright T E 1957 *J. Chem. Phys.* **27** 1208

[6] Allen M P and Tildesley D J 1990 *Computer Simulation of Liquids* (New York: Oxford University Press)

Frenkel D and Smit B 1996 *Understanding Molecular Simulation—From Algorithms to Applications* (San Diego, CA: Academic)

Binder K and Ciccotti G (ed) 1996 *Monte Carlo and Molecular Dynamics of Condensed Matter Systems* (Bolognia: Italian Physical Society)

Binder K and Heermann D W 1997 *Monte Carlo Simulation in Statistical Physics* (Berlin: Springer)

[7] Angell C A, Clarke J H R and Woodcock L V 1981 *Adv. Chem. Phys.* **48** 397

Barrat J-L and Klein M L 1991 *Annu. Rev. Phys. Chem.* **42** 23

[8] Poole P H, McMillan P F and Wolf G H 1995 *Structure, Dynamics and Properties of Silicate Melts* ed J F Stebbins, P F McMillan and D B Dingwell (Washington, DC: Mineralogical Society of America) p 563

Binder K and Kob W 1998 *Analysis of Composition and Structure of Glass and Glass Ceramics* ed H Bach and D Krause (Berlin: Springer) at press

Kob W and Binder K 1998 *Analysis of Composition and Structure of Glass and Glass Ceramics* ed H Bach and D Krause (Berlin: Springer) at press

[9] Wuttke J, Hernandez J, Li G, Coddens G, Cummins H Z, Fujara F, Petry W and Sillescu H 1994 *Phys. Rev. Lett.* **72** 3052

[10] Rössler E, Sokolov A P, Kisliuk A and Quitmann D 1994 *Phys. Rev.* B **49** 14 967

[11] Götze W 1991 *Liquids, Freezing and the Glass Transition (Les Houches Session LI, 1989)* ed J-P Hansen, D Levesque and J Zinn-Justin (North-Holland, Amsterdam) p 287

Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241

Kob W 1997 *Experimental and Theoretical Approaches to Supercooled Liquids: Advances and Novel Applications* ed J Fourkas, D Kivelson, U Mohanty and K Nelson (Washington, DC: ACS) p 28

[12] van Megen W and Pusey P N 1991 *Phys. Rev.* A **43** 5429

Bartsch E, Antonietti M, Schupp W and Sillescu H 1992 *J. Chem. Phys.* **97** 3950

van Megen W and Underwood S M 1994 *Phys. Rev.* E **49** 4206

[13] Fredrickson G H and Andersen H C 1985 *J. Chem. Phys.* **83** 5822

Fredrickson G H and Brawer S A 1986 *J. Chem. Phys.* **84** 3351

Weber T A, Fredrickson G H and Stillinger F H 1986 *Phys. Rev.* B **34** 7641

Ertel W, Froböse K and Jäckle J 1988 *J. Chem. Phys.* **88** 5027

Froböse K 1989 *J. Stat. Phys.* **55** 1285

Jäckle J, Froböse K and Knödler D 1991 *J. Stat. Phys.* **63** 249

Kob W and Andersen H C 1993 *Phys. Rev.* E **47** 3281

Kob W and Andersen H C 1993 *Phys. Rev.* **48** 4364

[14] Brüning R and Samwer K 1992 *Phys. Rev.* B **46** 11 318

[15] Angell C A 1985 *Relaxation in Complex Systems* ed K L Ngai and G B Wright (Springfield, DC: US Department of Commerce)

[16] Rieger H 1995 *Annual Reviews of Computational Physics* vol 2, ed D Stauffer (Singapore: World Scientific) p 295

[17] Young A P (ed) 1998 *Spin Glasses and Random Fields* (Singapore: World Scientific)

[18] Sherrington D 1999 *Proc. 1997 Canberra Summer School on The Physics of Novel Materials* at press (Sherrington D 1998 *Preprint* cond-mat/9806289)

[19] Kob W 1995 *Annual Reviews of Computational Physics* vol 3, ed D Stauffer (Singapore: World Scientific) p 1

[20] Gibbs J H and DiMarzio E A 1958 *J. Chem. Phys.* **28** 373

DiMarzio E A and Gibbs J H 1958 *J. Chem. Phys.* **28** 807

[21] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)

Balucani U and Zoppi M 1994 *Dynamics of the Liquid State* (Oxford: Oxford University Press)

[22] Ritort F 1995 *Phys. Rev. Lett.* **75** 1190

Franz S and Ritort F 1995 *Europhys. Lett.* **31** 507

Prados A, Brey J J and Sánchez-Rey B 1997 *Phys. Rev.* B **55** 6343

[23] Kurchan J, Peliti L and Sellitto M 1997 *Europhys. Lett.* **39** 365
[24] Signorini G F, Barrat J-L and Klein M L 1990 *J. Chem. Phys.* **92** 1294
     Sindzingre P and Klein M L 1992 *J. Chem. Phys.* **96** 4681
     Kudchadkar S R and Wiest J M 1995 *J. Chem. Phys.* **103** 8566
     Baschnagel J, Binder K and Wittmann H P 1993 *J. Phys.: Condens. Matter* **5** 1597
     Lobe B and Baschnagel J 1994 *J. Chem. Phys.* **101** 1616
     Renner C, Löwen H and Barrat J-L 1995 *Phys. Rev.* E **52** 5091
[25] Lewis L J and Wahnström G 1993 *Solid State Commun.* **86** 295
     Lewis L J and Wahnström G 1994 *Phys. Rev.* E **50** 3865
[26] Bennemann C, Paul W, Binder K and Dünweg B 1998 *Phys. Rev.* E **57** 843
[27] Kämmerer S, Kob W and Schilling R 1997 *Phys. Rev.* E **56** 5450
     Kämmerer S, Kob W and Schilling R 1998 *Phys. Rev.* E **58** 2131
     Kämmerer S, Kob W and Schilling R 1998 *Phys. Rev.* E **58** 2141
[28] Rustad J R, Yuen D A and Spera F R 1991 *Phys. Rev.* B **44** 2108
[29] Jin W, Kalia R K, Vashishta P and Rino J P 1993 *Phys. Rev. Lett.* **71** 3146
[30] Poole P H, Hemmati M and Angell C A 1997 *Phys. Rev. Lett.* **79** 2281
[31] Badro J, Gillet P and Barrat J-L 1998 *Europhys. Lett.* **42** 643
[32] Lacks D L 1998 *Phys. Rev. Lett.* **80** 5385
[33] Baschnagel J and Binder K 1995 *Macromolecules* **28** 6808
[34] Fehr T and Löwen H 1995 *Phys. Rev.* E **52** 4016
[35] Sciortino F, Poole P H, Essmann U and Stanley H E 1997 *Phys. Rev.* E **55** 727
     Tanaka H 1998 *Phys. Rev. Lett.* **80** 113
[36] Badro J, Teter D M, Downs R T, Gillet P, Hemley R J and Barrat J-L 1997 *Phys. Rev.* B **56** 5797
[37] Sarnthein J, Pasquarello A and Car R 1995 *Phys. Rev. Lett.* **74** 4682
     Pasquarello A, Sarnthein J and Car R 1998 *Phys. Rev.* B **57** 14 133
[38] Pasquarello A and Car R 1998 *Phys. Rev. Lett.* **80** 5145
[39] Swope W C and Andersen H C 1990 *Phys. Rev.* B **41** 7042
     Vashishta P, Kalia R K, Li W, Nakano A, Omeltchenko A, Tsuruta K, Wang J H and Ebbsjö I 1996 *Curr. Opinion Solid State Mater. Sci.* **1** 853
[40] Horbach J, Kob W, Binder K and Angell C A 1996 *Phys. Rev.* E **54** R5897
[41] Buchenau U, Prager M, Nücker N, Dianoux A J, Ahmad N and Phillips W A 1986 *Phys. Rev.* B **34** 5665
     Benassi P, Krisch M, Masciovecchio C, Mazzacurati V, Monaco G, Ruocco G, Sette F and Verbeni R 1996 *Phys. Rev. Lett.* **77** 3835
     Foret M, Courtens E, Vacher R and Suck J-B 1996 *Phys. Rev. Lett.* **77** 3831
     Schirmacher W, Diezemann G and Ganter C 1998 *Phys. Rev. Lett.* **81** 136
     Wischnewski A, Buchenau U, Dianoux A J, Kamitakahara W A and Zarestky J L 1998 *Phys. Rev.* B **57** 2663
[42] Taraskin S N and Elliott S R 1997 *Europhys. Lett.* **39** 37
     Taraskin S N and Elliott S R 1997 *Phys. Rev.* B **56** 8605
[43] See, e.g., Sokal A D 1995 *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* ed K Binder (New York: Oxford University Press) p 47
[44] Dress C and Krauth W 1995 *J. Phys. A: Math. Gen.* **28** L597
     Krauth W and Pluchery O 1994 *J. Phys. A: Math. Gen.* **27** L715
     Achenbach M 1996 *Diploma Thesis* University of Mainz
     Barkema G T and Mousseau N 1996 *Phys. Rev. Lett.* **77** 4358
     Dittes F-M 1996 *Phys. Rev. Lett.* **76** 4651
     Hansmann U H E and Okamoto Y 1997 *Phys. Rev.* E **56** 2228
     Huber G A and McCammon J A 1997 *Phys. Rev.* E **55** 4822
     Bhattacharya K K and Sethna J P 1998 *Phys. Rev.* E **57** 2553
     Doye J P K and Wales D J 1998 *Phys. Rev. Lett.* **80** 1357
     Steiner M M, Genilloud P-A and Wilkins J W 1998 *Phys. Rev.* B **57** 10 236
[45] Schmidt-Rohr K and Spiess H W 1991 *Phys. Rev. Lett.* **66** 3020
     Böhmer R, Hinze G, Diezemann G, Geil B and Sillescu H 1995 *Europhys. Lett.* **36** 55
     Heuer A, Wilhelm M, Zimmermann H and Spiess H W 1995 *Phys. Rev. Lett.* **95** 2851
     Cicerone M T, Blackburn F R and Ediger M D 1995 *J. Chem. Phys.* **102** 471
     Cicerone M T and Ediger M D 1996 *J. Chem. Phys.* **104** 7210
     Sillescu H 1999 *J. Non-Cryst. Solids* at press
[46] Butler S and Harrowell P 1991 *J. Chem. Phys.* **95** 4466
     Heuer A and Okun K 1997 *J. Chem. Phys.* **106** 6176

Kob W, Donati C, Plimpton S J, Glotzer S C and Poole P H 1997 *Phys. Rev. Lett.* **79** 2827
Donati C, Douglas J F, Kob W, Plimpton S J, Poole P H and Glotzer S C 1998 *Phys. Rev. Lett.* **80** 2338
Doliva B and Heuer A 1998 *Phys. Rev. Lett.* **80** 4915
Glotzer S C, Jan N, Lookman T, MacIsaac A B and Poole P H 1998 *Phys. Rev.* E **57** 7350
Muranaka T and Hiwatari Y 1998 *J. Phys. Soc. Japan* **67** 1982
Yamamoto R and Onuki A 1998 *Phys. Rev. Lett.* **81** 4915
(Yamamoto R and Onuki A 1998 *Preprint* cond-mat/9806207)
Yamamoto R and Onuki A 1998 *Phys. Rev.* E **58** 3515
(Yamamoto R and Onuki A 1998 *Preprint* cond-mat/9807180)
Yamamoto R and Onuki A 1997 *J. Phys. Soc. Japan* **66** 2545
(Yamamoto R and Onuki A 1998 *Preprint* cond-mat/9807218)
[47] Dasgupta C, Indrani A V, Ramaswamy S and Phani M K 1991 *Europhys. Lett.* **15** 307
Ernst R M, Nagel S R and Grest G S 1991 *Phys. Rev.* B **43** 8070
Binder K, Baschnagel J, Böhmer S and Paul W 1998 *Phil. Mag.* B **77** 591
[48] Habasaki J, Okada I and Hiwatari Y 1995 *Phys. Rev.* E **52** 2681
[49] Horbach J, Kob W and Binder K 1999 *J. Non-Cryst. Solids* **235–237** 320
[50] Dell'Anna R, Ruocco G, Sampoli M and Viliani G 1998 *Phys. Rev. Lett.* **80** 1236
[51] Maass P, Bunde A and Ingram M D 1992 *Phys. Rev. Lett.* **68** 3064
Balasubramanian S and Rao K J 1993 *J. Phys. Chem.* **97** 8835
Habasaki J, Okada I and Hiwatari Y 1996 *J. Non-Cryst. Solids* **208** 181
[52] Rino J P, Ebbsjö I, Kalia R K, Nakano A and Vashishta P 1993 *Phys. Rev.* B **47** 3053
[53] Vollmayr K and Kob W 1996 *Ber. Bunsenges. Phys. Chem.* **100** 1399
[54] Vollmayr K, Kob W and Binder K 1996 *Phys. Rev.* B **54** 15 808
[55] Takada A, Catlow C R A and Price G D 1995 *J. Phys.: Condens. Matter* **7** 8659
Takada A, Catlow C R A and Price G D 1995 *J. Phys.: Condens. Matter* **7** 8693
[56] Tsuneyuki S, Tsukada M, Aoki H and Matsui Y 1988 *Phys. Rev. Lett.* **61** 869
[57] van Beest B W H, Kramer G J and van Santen R A 1990 *Phys. Rev. Lett.* **64** 1955
[58] Kramer G J, de Man A J M and van Santen R A 1991 *J. Am. Chem. Soc.* **113** 6435
[59] Gonze X, Charlier J-C, Allan D C and Teter M P 1994 *Phys. Rev.* B **50** 13 035
[60] Wilson M and Madden P A 1994 *Phys. Rev. Lett.* **72** 3033
[61] Hemmati M and Angell C A 1998 *Physics meets Geology* ed H Aoki and R Hemley (Cambridge: Cambridge University Press)
[62] Vessal B, Amini M, Fincham D and Catlow C R A 1989 *Phil. Mag.* B **60** 753
[63] Della Valle R G and Venuti E 1994 *Chem. Phys.* **179** 411
Della Valle R G and Andersen H C 1991 *J. Chem. Phys.* **94** 5056
Guissani Y and Guillot B 1996 *J. Chem. Phys.* **104** 7633
[64] Horbach J, Kob W and Binder K 1998 *Phil. Mag.* B **77** 297
[65] Ullo J J and Yip S 1985 *Phys. Rev. Lett.* **54** 1509
Ullo J J and Yip S 1989 *Phys. Rev.* A **39** 5877
Ullo J J and Yip S 1990 *Chem. Phys.* **149** 221
[66] Bernu B, Hiwatari Y and Hansen J-P 1985 *J. Phys. C: Solid State Phys.* **18** L371
Bernu B, Hansen J-P, Hiwatari Y and Pastore G 1987 *Phys. Rev.* A **36** 4891
Pastore G, Bernu B, Hansen J-P and Hiwatari Y 1988 *Phys. Rev.* A **38** 454
Miyagawa H, Hiwatari Y, Bernu B and Hansen J-P 1988 *J. Chem. Phys.* **88** 3879
Roux J-N, Barrat J-L and Hansen J-P 1989 *J. Phys.: Condens. Matter* **1** 7171
Barrat J-L, Roux J-N and Hansen J-P 1990 *Chem. Phys.* **149** 197
[67] Miyagawa H and Hiwatari Y 1989 *Phys. Rev.* A **40** 6007
Miyagawa H and Hiwatari Y 1991 *Phys. Rev.* A **44** 8278
Hiwatari Y, Matsui J, Uehara K, Muranaka T, Miyagawa H, Takasu M and Odagaki T 1994 *Physica* A **204** 306
Matsui J, Odagaki T and Hiwatari Y 1994 *Phys. Rev. Lett.* **73** 2452
[68] Hurley M M and Harrowell P 1995 *Phys. Rev.* E **52** 1694
Hurley M M and Harrowell P 1996 *J. Chem. Phys.* **105** 10 521
[69] Parisi G 1997 *J. Phys. A: Math. Gen.* **30** L765
Parisi G 1997 *J. Phys. A: Math. Gen.* **30** 8523
Coluzzi B and Parisi G 1998 *J. Phys. A: Math. Gen.* **31** 4349
[70] Parisi G 1997 *Phys. Rev. Lett.* **79** 3660
[71] Wahnström G 1991 *Phys. Rev.* A **44** 3752
[72] Kob W and Andersen H C 1994 *Phys. Rev. Lett.* **73** 1376

Kob W and Andersen H C 1995 *Transport Theory Stat. Phys.* **24** 1179

Kob W and Andersen H C 1995 *Phys. Rev.* E **52** 4134

[73] Kob W and Andersen H C 1995 *Phys. Rev.* E **51** 4626

[74] See, e.g., Cape J N and Woodcock L V 1980 *J. Chem. Phys.* **72** 976

[75] Deserno M and Holm C 1998 *Preprint* cond-mat/9807099

Deserno M and Holm C 1998 *Preprint* cond-mat/9807100

[76] Greengard L and Rokhlin V 1987 *J. Comput. Phys.* **73** 325

Solvason D, Kolafa J, Petersen H G and Perram J W 1995 *Comput. Phys. Commun.* **87** 307

[77] Horbach J 1998 *PhD Thesis* University of Mainz

[78] Horbach J, Kob W and Binder K, unpublished

Horbach J and Kob W 1999 *Preprint* cond-mat/9901067

[79] Weber H, Paul W, Kob W and Binder K 1997 *Phys. Rev. Lett.* **78** 2136

[80] Angell C A, Poole P H and Shao J 1994 *Nuovo Cimento* D **16** 993

[81] Götze W and Sjögren L 1987 *Z. Phys.* B **65** 415

[82] Brébec G, Seguin R, Sella C, Bevenot J and Martin J C 1980 *Acta Metall.* **28** 327

Mikkelsen J C 1984 *Appl. Phys. Lett.* **45** 1187

[83] Gallo P, Sciortino F, Tartaglia P and Chen S-H 1996 *Phys. Rev. Lett.* **76** 2730

Chen S-H, Gallo P, Sciortino F and Tartaglia P 1997 *Phys. Rev.* E **56** 4231

Sciortino F, Fabbian L, Chen S-H and Tartaglia P 1997 *Phys. Rev.* E **56** 5397

[84] Rössler E and Sokolov A P 1996 *Chem. Geol.* **128** 143

Hess K U, Dingwell D B and Rössler E 1996 *Chem. Geol.* **128** 155

[85] Speedy R J 1997 *J. Chem. Phys.* **107** 3222

[86] Angell C A 1981 *Water: A Comprehensive Treatise* ed F Franks (New York: Plenum)

Lang E W and Lüdemann H D 1981 *Ber. Bunsenges. Phys. Chem.* **85** 603

[87] Teichler H 1996 *Phys. Rev. Lett.* **76** 62

[88] Clarke J H R 1995 *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* ed K Binder (New York: Oxford University Press) p 272

[89] Paul W and Baschnagel J 1995 *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* ed K Binder (New York: Oxford University Press) p 307

[90] See, e.g., the articles in *J. Res. Natl Inst. Standards Technol.* 1997 **102** (March–April) and the bibliography therein

[91] Wolfgardt M, Baschnagel J, Paul W and Binder K 1996 *Phys. Rev.* E **54** 1535

[92] Sjögren L 1980 *Phys. Rev.* A **22** 2866 and the bibliography therein

[93] Nauroth M and Kob W 1997 *Phys. Rev.* E **55** 657

[94] Gleim T, Kob W and Binder K 1998 *Phys. Rev. Lett.* **81** 4404

(Gleim T, Kob W and Binder K 1998 *Preprint* cond-mat/9805200)

[95] Löwen H, Hansen J-P and Roux J-N 1991 *Phys. Rev.* A **44** 1169

[96] Gleim T 1999 *PhD Thesis* University of Mainz

[97] Horbach J, Kob W and Binder K 1999 *Phys. Chem.* B at press

(Horbach J, Kob W and Binder K 1998 *Preprint* cond-mat/9809229)

[98] Struik L C E 1978 *Physical Aging in Amorphous Polymers and Other Materials* (Amsterdam: Elsevier)

McKenna G B 1989 *Polymer Properties (Comprehensive Polymer Science vol 12)* ed C Booth and C Price (Oxford: Pergamon) p 311

[99] Bouchaud J-P, Cugliandolo L F, Kurchan J and Mézard M 1996 *Physica* A **226** 243

Bouchaud J-P, Cugliandolo L F, Kurchan J and Mézard M 1998 *Spin Glasses and Random Fields* ed A P Young (Singapore: World Scientific) p 161

[100] Ciuchi S and de Pasquale F 1988 *Nucl. Phys.* B **300** 31

Cugliandolo L F and Kurchan J 1993 *Phys. Rev. Lett.* **71** 173

Cugliandolo L F, Kurchan J and Parisi G 1994 *J. Physique* I **4** 1641

Bouchaud J P and Dean D S 1995 *J. Physique* I **5** 265

Monthus C and Bouchaud J-P 1996 *J. Phys. A: Math. Gen.* **29** 3847

Yoshino H 1997 *J. Phys. A: Math. Gen.* **30** 1143

Cugliandolo L F and Kurchan J 1998 *Preprint* cond-mat/9807226

[101] Nieuwenhuizen Th M 1998 *Preprint* cond-mat/9807161

[102] Fisher D S and Huse D A 1988 *Phys. Rev.* B **38** 373

Koper G J M and Hilhorst H J 1988 *J. Physique* **49** 429

[103] Lundgren L, Svedlindh P, Nordblad P and Beckman O 1983 *Phys. Rev. Lett.* **51** 911

Alba M, Vincent E, Hammann J and Ocio M 1987 *J. Appl. Phys.* **61** 4092

Vincent E, Bouchaud J-P, Dean D S and Hammann J 1995 *Phys. Rev.* B **52** 1050
Djurberg C, Mattson J and Nordblad P 1995 *Europhys. Lett.* **29** 163
[104] Rieger H 1993 *J. Phys. A: Math. Gen.* **26** L615
Rieger H 1994 *J. Physique* I **4** 883
Rieger H, Steckemetz B and Schreckenberg M 1994 *Europhys. Lett.* **27** 485
Franz S and Rieger H 1995 *J. Stat. Phys.* **79** 749
Alvarez D, Franz S and Ritort F 1996 *Phys. Rev.* B **54** 9756
Kisker J, Santen L, Schreckenberg M and Rieger H 1996 *Phys. Rev.* B **53** 6418
Marinari E, Parisi G, Ricci-Tersenghi F and Ruiz-Lorenzo J J 1998 *J. Phys. A: Math. Gen.* **31** 2611
[105] Barrat A 1997 *Phys. Rev.* E **55** 5651
Barrat A 1998 *Phys. Rev.* E **57** 3629
Yoshino H 1998 *Preprint* cond-mat/9802283
[106] Chandra P, Feigelman M V, Ioffe L B and Kagan D M 1997 *Phys. Rev.* B **56** 11 553
Frachebourg L, Krapivsky P L and Redner S 1997 *Phys. Rev.* E **55** 6684
Godrèche C and Luck J M 1997 *J. Phys. A: Math. Gen.* **30** 6245
Prados A, Brey J J and Sánchez-Rey B 1997 *Europhys. Lett.* **40** 13
[107] Alberici F, Doussineau P and Levelut A 1997 *Europhys. Lett.* **39** 329
Salmon E, Ausloos M and Vandewalle N 1997 *Phys. Rev.* E **55** R6348
Leheny R L and Nagel S R 1998 *Phys. Rev.* B **57** 5154
Bonn D, Tanaka H, Wegdam G, Kellay H and Meunier J 1998 *Preprint*
[108] Kob W and Barrat J-L 1997 *Phys. Rev. Lett.* **78** 4581
[109] Barrat J-L and Kob W 1998 *Preprint* cond-mat/9806027
[110] Andrejew E and Baschnagel J 1996 *Physica* A **233** 117
[111] Kob W and Barrat J-L 1998 *Preprint* cond-mat/9807364
[112] Baschnagel J 1994 *Phys. Rev.* B **49** 135
[113] Cugliandolo L F, Kurchan J and Peliti L 1997 *Phys. Rev.* E **55** 3898
[114] Tool A Q and Eichlin C G 1931 *J. Opt. Soc. Am.* **14** 276
[115] Weber T A and Stillinger F H 1985 *Phys. Rev.* B **31** 1954
Weber T A and Stillinger F H 1985 *Phys. Rev.* B **32** 5402
Keyes T 1994 *J. Chem. Phys.* **101** 5081
Laird B B and Schober H R 1991 *Phys. Rev. Lett.* **66** 636
Schober H R and Laird B B 1991 *Phys. Rev.* B **44** 6746
Bembenek S and Laird B B 1995 *Phys. Rev. Lett.* **74** 936
Bembenek S and Laird B B 1996 *J. Chem. Phys.* **104** 5199
Gezelter J D, Rabani E and Berne B J 1997 *J. Chem. Phys.* **107** 4618
Keyes T, Vijayadamodar G V and Zurcher U 1997 *J. Chem. Phys.* **106** 4651