ELSEVIER

Journal of Non-Crystalline Solids 307–310 (2002) 181–187

JOURNAL OF NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Quantitative tests of mode-coupling theory for fragile and strong glass formers

Walter Kob [a,*], Markus Nauroth [b], Francesco Sciortino [c]

[a] *Laboratoire des Verres, Université Montpellier II, F-34095 Montpellier, France*
[b] *Institut für Physik, Johannes–Gutenberg–Universität, Staudinger Weg 7, D–55099 Mainz, Germany*
[c] *Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Universitá di Roma La Sapienza, P.le Aldo Moro 2, I-00185 Rome, Italy*

Abstract

We calculate for a binary mixture of Lennard-Jones particles the time dependence of the solution of the mode-coupling equations in which the full wave vector dependence is taken into account. In addition we also take into account the short time dynamics, which we model with a simple memory kernel. We find that the so obtained solution agrees very well with the time and wave vector dependence of the coherent and incoherent intermediate scattering functions as determined from molecular dynamics computer simulations. Furthermore we calculate the wave vector dependence of the Debye–Waller factor for a realistic model of silica and compare these results with the ones obtained from a simulation of this model. We find that if the contribution of the three point correlation function to the vertices of the memory kernel are taken into account, the agreement between theory and simulation is very good. Hence we conclude that mode coupling theory is able to give a correct quantitative description of the caging phenomena in fragile as well as strong glass-forming liquids.

PACS: 61.43.Fs; 61.20.Lc; 02.70.Ns; 64.70.Pf

1. Introduction

In the last decade our understanding of the dynamics of supercooled liquids has made significant progress [1]. In particular it has been shown that for fragile glass formers the bend one observes if one plots the logarithm of the viscosity as a function of the inverse temperature can be explained very well by means of the so-called mode-coupling theory of the glass transition (MCT) [2]. In the vicinity of this bend the dynamics of the system changes qualitatively in that the particles start to experience strong caging effects, i.e. they are temporarily trapped by the particles that surround them. MCT gives a self-consistent description of the dynamics of the particles inside this cage as well as how the particles leave this cage, i.e. of the structural relaxation of the supercooled liquid. In the past the predictions of this theory have been checked in many experiments as well as computer simulations and it was found that MCT

* Corresponding author. Tel.: +33-4 67 14 93 26; fax: +33-4 67 14 34 98.
E-mail address: kobe@ldv.univ-montp2.fr (W. Kob).

0022-3093/02/$ - see front matter
PII: S0022-3093(02)01457-6

is indeed able to give a qualitatively correct description of the relaxation dynamics [2].

However, in principle the theory is supposed to give not only a qualitative description of the relaxation dynamics of supercooled liquids, but also a quantitative one, *if* the static properties of the system are known with sufficiently high precision. This attractive feature originates directly from the way the theory is (or can be) derived, namely the Mori–Zwanzig formalism in which one obtains equations of motion for slow variables which involve their *static* values. Thus, once these static values are known one can, in principle, determine their time dependence. In particular it is possible to calculate from the knowledge of the static structure factor the time dependence of the coherent and incoherent intermediate scattering functions, $F(q,t)$ and $F_s(q,t)$, respectively, where q is the wave vector. Unfortunately, in the past these types of calculations have been done only for very few systems, since on the one hand they are quite involved and on the other hand they require as input structural data with very high quality (better than 1%) [3–9]. In the present paper we expand these type of calculations in two directions. On the one hand we solve for a simple glass-forming system, a binary Lennard-Jones mixture (BMLJ), the full time and wave vector dependence of the MCT equations, including a realistic short time dynamics, and compare them with results from computer simulations of the same system. On the other hand we calculate the q-dependence of the nonergodicity parameters (NEP) for silica (SiO_2), a glass former whose structure is given by an open tetrahedral network and who is the prototype of a strong glass former, and compare also these results with the ones from simulations of the same system.

2. Theory

In this section we summarize the MCT equations that are needed to calculate the quantities discussed in Section 4. In order to keep this presentation as simple as possible we will discuss only the equation for the case of a one-component system, although in reality we have used the equations for a two-component system, since the BMLJ as well as SiO_2 belong to this class. The full binary equations can be found in Refs. [3,10,11].

The intermediate scattering function can be defined by $F(q,t) = \langle \delta\rho(\mathbf{q},0)\delta\rho(\mathbf{q},t)\rangle$ where $\delta\rho$ are the density fluctuations. $F(q,t)$ obeys the exact equation of motion

$$\ddot{F}(q,t) + \Omega^2(q)F(q,t) + \int_0^t M(q,\tau)\dot{F}(q,t-\tau)\,\mathrm{d}\tau = 0, \tag{1}$$

where the frequency Ω is given by $\Omega^2 = q^2 k_B T/(mS(q))$. Here m and $S(q)$ are the mass of the particles and the static structure factor respectively. The function $M(q,t)$ in Eq. (1) is the so-called memory function and it is useful to write it as follows:

$$M(q,t) = M^{\mathrm{REG}}(q,t) + \left\{M^{\mathrm{MCT}}[F(k,t)](q) - M^{\mathrm{MCT}}[F^B(k,t)](q)\right\}. \tag{2}$$

Here $M^{\mathrm{REG}}(q,t)$ is that part of the memory function which is responsible for the dynamics of the system at very short times, i.e. after the particles have left the ballistic regime. The functional $M^{\mathrm{MCT}}[F(k,t)]$ is the usual memory kernel of MCT which depends on the static structure factor as well as on the three point correlation function $c_3(\mathbf{q},\mathbf{k})$ [2]. Also it contains a short time part. But since we want to describe this time regime by means of $M^{\mathrm{REG}}(q,t)$, we have to subtract out this part from $M^{\mathrm{MCT}}[F(k,t)]$. This is done in the last term of Eq. (2), where F^B is a function which decays rapidly to zero, but has the correct behavior at short times [10].

For the regular memory function $M^{\mathrm{REG}}(q,t)$ one can make different type of Ansatzes. One which seems to work well at high temperatures is given by [12]

$$M^{\mathrm{REG}}(q,t) = \alpha(q)/\cosh(\beta(q)t). \tag{3}$$

Here $\alpha(q)$ and $\beta(q)$ are parameters which can be calculated via sum rules from the static structure factor and other static quantities which can be measured in a computer simulation [10,13]. Hence they are *not* adjustable fit parameters.

Eqs. (1)–(3) are a self-contained set of equations of motion from which one thus can calculate the full time and wave vector dependence of $F(q,t)$, and similar equations exist for the incoherent

intermediate scattering function $F_s(q,t)$. We have solved these equations by discretizing q-space into 100 points that covered the q-range up to three to four times the location of the main peak in $S(q)$.

3. Models and details of the simulations

The first model investigated is a 80:20 mixture of Lennard-Jones particles. In the following we will call the majority and minority species A and B particles, respectively. Both of them have the same mass m and they interact via a potential $V_{\alpha\beta} = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}]$, $\alpha,\ \beta \in \{\mathrm{A},\mathrm{B}\}$. The parameters $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are given by $\epsilon_{\mathrm{AA}} = 1.0$, $\sigma_{\mathrm{AA}} = 1.0$, $\epsilon_{\mathrm{AB}} = 1.5$, $\sigma_{\mathrm{AB}} = 0.8$, $\epsilon_{\mathrm{BB}} = 0.5$, and $\sigma_{\mathrm{BB}} = 0.88$. This potential is truncated and shifted at a distance $\sigma_{\alpha\beta}$. In the following we will use σ_{AA} and ϵ_{AA} as the unit of length and energy, respectively (setting the Boltzmann constant $k_{\mathrm{B}} = 1.0$). Time will be measured in units of $\sqrt{m\sigma_{\mathrm{AA}}^2/48\epsilon_{\mathrm{AA}}}$. In the past the structural and dynamical properties of this system have been studied in great detail [14,15]. More detail on this can be found in Ref. [16].

For the present work we only needed to determine the three point correlation function c_3 since the time and temperature dependence of $F(q,t)$ and $F_s(q,t)$, as well as the one of $S(q)$, can be found in the mentioned literature. For this we simulated a system of 800 A particles and 200 B particles in a box with volume $(9.4)^3$. The total time of this simulation was about 10^8 time steps from which we obtained roughly 12,000 independent configurations. This large number was necessary to determine c_3 with sufficient precision. Due to this large computational effort we did this calculation only for one temperature, $T = 1.0$. Thus in the following we will assume that the temperature dependence of c_3 is weak.

The second model we study is amorphous silica, SiO_2. For this we use the potential proposed by van Beest et al. which has the functional form [17]

$$\phi_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta}\exp(-B_{\alpha\beta}r) - \frac{C_{\alpha\beta}}{r^6} \qquad \alpha,\beta \in [\mathrm{Si},\mathrm{O}]. \tag{4}$$

The values of the constants $q_\alpha, q_\beta, A_{\alpha\beta}, B_{\alpha\beta}$, and $C_{\alpha\beta}$ can be found in Ref. [17]. The potential has been truncated and shifted at 5.5 Å. In the past it has been shown that this potential is able to give a reliable description of silica in its molten phase as well as in the glass (see [18–20] and references therein). For the present calculations to determine c_3 we used 600 ions in a box with volume $(20.4\ \text{Å})^3$. The total length of the simulation was 2×10^7 time steps, from which we obtained at 4000 K around 2000 independent configurations.

4. Results

We start by considering first the dynamics of the BMLJ at intermediate and high temperatures. In this T-range it can be expected that the effect of the memory kernel of MCT is not relevant and thus we will set it to zero. In Fig. 1 we show the time dependence of $F_{\mathrm{AA}}(q,t)$ for various temperatures. The wave vector is 7.25, the location of the main peak in $S_{\mathrm{AA}}(q)$. The dashed lines with symbols are the result of the simulation whereas the full lines are the prediction of the theory. As can be seen, the theory works very well at high temperatures but starts to break down at intermediate

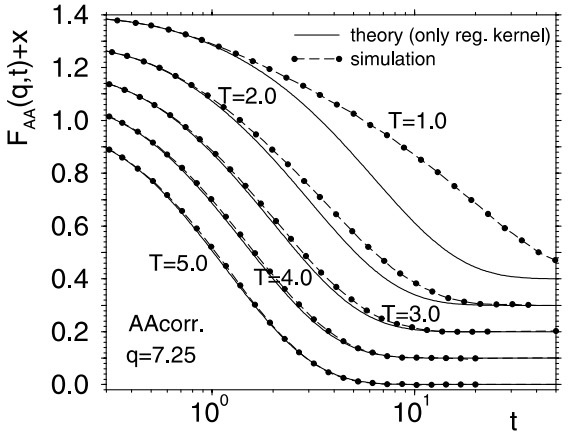

Fig. 1. Time dependence of the coherent intermediate scattering function for the A particles in the BMLJ system for different temperatures as obtained from the simulation (dashed lines with symbols) and as predicted from the theory if the MCT kernel is not taken into account (solid lines). For clarity some of the curves have been shifted vertically.

temperatures in that it underestimated the correlation function at intermediate times. Thus we see that even at the intermediate temperature $T = 1.0$, which is more than twice the MCT temperature $T_c = 0.435$, cage effects become important.

In order to see whether the memory kernel M^{MCT} is able to take into account these effects we have solved Eqs. (1)–(3) by taking now into account also this contribution to the memory function $M(q,t)$. In doing this we had to face a problem which we had encountered already some time ago [7], namely that MCT is not able to predict reliably the value of the critical temperature T_c. For the BMLJ the simulations show that $T_c \approx 0.435$ [14], whereas the theory predicts a value around 0.92 [7]. This means that the theory is not able to predict correctly the *absolute* value of the time scale for the α-relaxation, although it is able to predict the shape of the correlation functions (see below). Therefore we had to use *one* adjustable parameter, a temperature which we will denote by T_f, which is the temperature at which the vertices in the MCT-functional M^{MCT} are evaluated. The value of T_f was adjusted such that the time scale for $F_{\mathrm{AA}}(q,t)$ for $q = 7.25$ was reproduced correctly.

In Fig. 2 we show the time dependence of the coherent as well as the incoherent intermediate scattering function for $q = 7.25$ and 9.98, the location of the first peak and the first minimum in $S_{\mathrm{AA}}(q)$, respectively. The temperature is 2.0, i.e. a value for which we find that the *regular* memory kernel is no longer able to give a good description of the relaxation dynamics (see Fig. 1). From this figure we see that in general the agreement between the simulation and the theory is very good in that the shape of the curves as well as their position is correctly predicted. (The discrepancy found for $F_{\mathrm{AA}}(q = 9.98, t)$, where the theory predicts a pronounced shoulder at around $t = 2$ whereas the simulation shows only a weak shoulder in that time regime, is probably related to the fact that the description of the short time dynamics is not yet completely adequate [10].) Thus we conclude that MCT is indeed able to give a correct description of the relaxation dynamic of the system at intermediate temperatures, i.e. at temperatures where the cage effect starts to become noticeable.

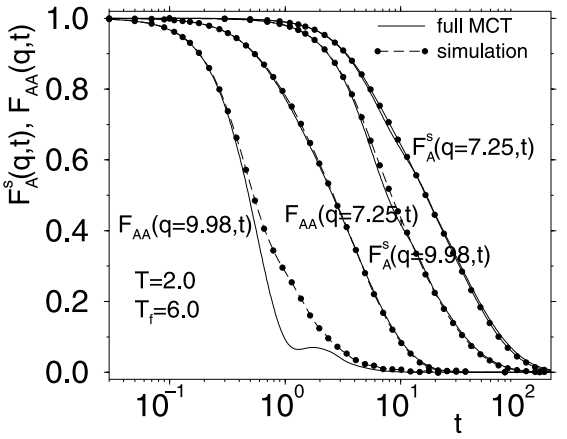

Fig. 2. Time dependence of the coherent and incoherent intermediate scattering function of the BMLJ system for two wave vectors at $T = 2.0$. The dashed line with the symbols are the results from the simulation and the solid lines are the prediction of the theory in which the MCT kernel has been taken into account.

We now check whether this conclusion is also correct if the temperature is so low that the cage effect becomes very important. For this we have solved the MCT equations for $T = 0.466$, i.e. a temperature for which the relaxation dynamics is about 10^4 times slower than the one at high T. The time dependence of $F_{\mathrm{AA}}(q,t)$ and of $F^s_{\mathrm{A}}(q,t)$ as predicted from the theory is shown in Fig. 3. Also included are the results from the computer simulations from Ref. [14]. As in the case of interme-

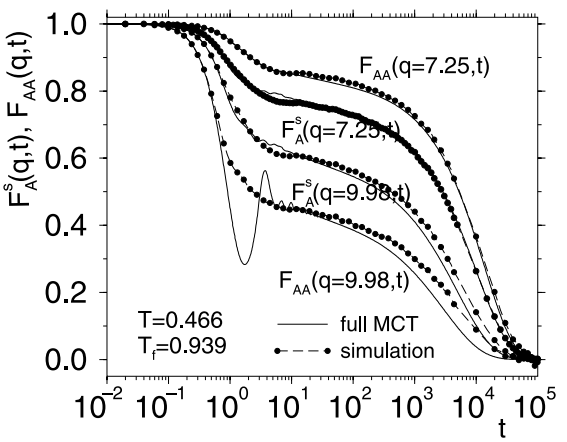

Fig. 3. Same as Fig. 2 but now for $T = 0.466$.

diate temperatures, Fig. 2, we find that also for this T the agreement between theory and simulation is very good. The main discrepancy is again seen for $F_{AA}(q,t)$ at $q = 9.98$, and the reason for it is the same as the one given above. All in all we thus conclude that for this system the theory is indeed able to predict the full time and wave vector dependence of the coherent and incoherent scattering function.

The temperature dependence of the relaxation time of the BMLJ system shows significant deviations from an Arrhenius law [14]. As mentioned above, these deviations are believed to be related to a change in the transport mechanism of the particles which show a hopping type of motion at low temperatures whereas at high T they show a more collective/flow-like behavior. It is of interest that recently it has been suggested that even silica shows such a crossover in the transport mechanism, although this crossover occurs at relatively high temperatures (around 3300 K) [18]. Therefore one might ask whether MCT is able to give a reliable description of the relaxation dynamics of this important glass-forming system also. Note that from a structural point of view the BMLJ system and amorphous silica are very different, since the former one resembles the random close packing of hard spheres whereas the latter is given by an open network structure similar to the continuous random tetrahedral network proposed long time ago by Zachariasen [21]. Since, as pointed out in Section 1, MCT uses only structural information to predict the dynamics, it is of great interest to see whether the theory is also able to give a correct quantitative description if the structure is very different from the one of closed packed hard spheres.

To check this we have calculated for amorphous silica the wave vector dependence of the NEPs, i.e. the height of the plateau in the intermediate scattering function at intermediate times (see, e.g., Fig. 3). Before we discuss the results, we have to mention a technical point which makes the calculation of the NEP for the case of silica much harder than for the case of the BMLJ. In Section 2 we mentioned that the memory kernel of the MCT contains only static quantities, namely the static structure factor $S(q)$ and the three point correlation function $c_3(\mathbf{q},\mathbf{k})$. From a simulation it is quite easy to determine $S(q)$ with high precision. For the function c_3 this is, however, not the case, since due to the two vectorial arguments the statistics for this quantity are very bad. Therefore we had to make very long simulations in order to determine c_3 with sufficient accuracy. More details on this can be found in Ref. [11].

In the following we will discuss the results for the NEP for the BMLJ as well as for the case of silica. Since all of the results presented in Figs. 1–3 were obtained with the approximation that $c_3 \equiv 0$, one has of course to check whether or not they do not change if this assumption is not made. We mention, however, already here, that some time ago Barrat et al. showed that this approximation is very good for the case of a soft-sphere system, i.e. a system which is relatively similar to the BMLJ considered here [22]. Whether this result holds also for the case of a system with an open network structure has, however, so far not been investigated. We also mention that in order to calculate the NEPs it is not necessary to introduce any fit parameter of any kind. The only input to the data are the partial structure factors [2]. Thus for this type of calculation the above discussed problem with the T_f does not exist.

In Fig. 4 we show the wave vector dependence of the NEP for the coherent functions. (Note that since this is a binary system, there are three of them. Furthermore we mention that for reasons of convenience we show the NEP multiplied by the corresponding partial structure factors.) In each panel we show three curves: The circles are the result from the simulation published in Ref. [15]. The dashed and full line is the theoretical result for the cases that c_3 is set equal to zero and $c_3 \neq 0$, respectively. First of all this figure shows that the theory is able to reproduce with excellent accuracy the data of the simulation without any adjustable parameter. Furthermore we recognize from Fig. 4 also that the theoretical prediction hardly depends on whether or not c_3 is taken into account, in agreement with the finding of Barrat et al. [22].

For silica the situation is quite different as can be inferred from Fig. 5 where we show the wave vector dependence of the NEP for this system. We see that in this case the theoretical prediction for

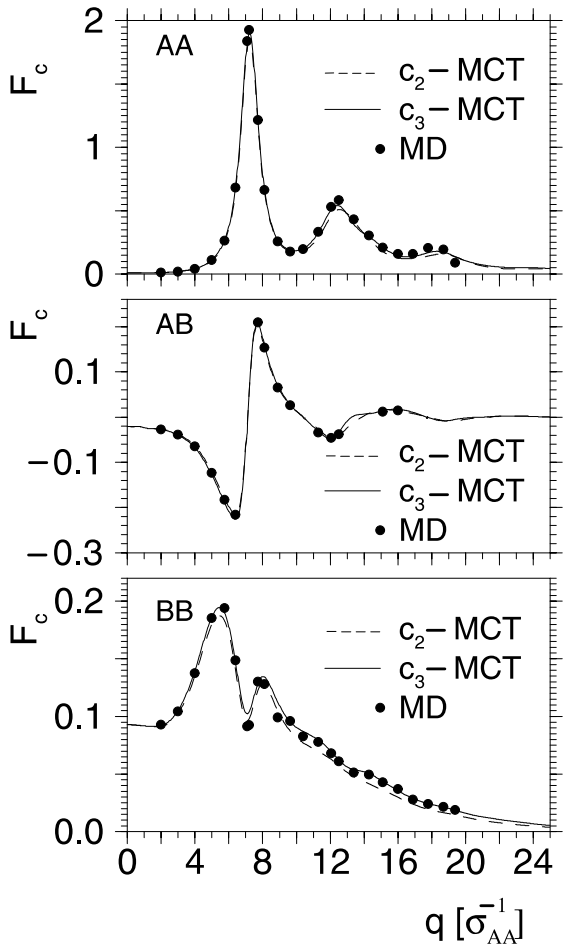

Fig. 4. Wave vector dependence of the NEPs for the BMLJ system. The circles are the result of the simulation, the dashed line is the theoretical prediction if the three point correlation function is set to zero, and the full line is the theoretical prediction if this function is taken into account.

$c_3 = 0$ differs strongly from the one if this function is taken into account. Thus we find that for the case of a network structure the contribution of the three point correlation function to the memory function is very important. It is remarkable that if the contributions of c_3 are taken into account, the theoretical prediction agrees very well with the result of the simulation, which were presented in Ref. [19]. Thus we conclude that the theory is also able to give a quantitative correct prediction for this type of glass former.

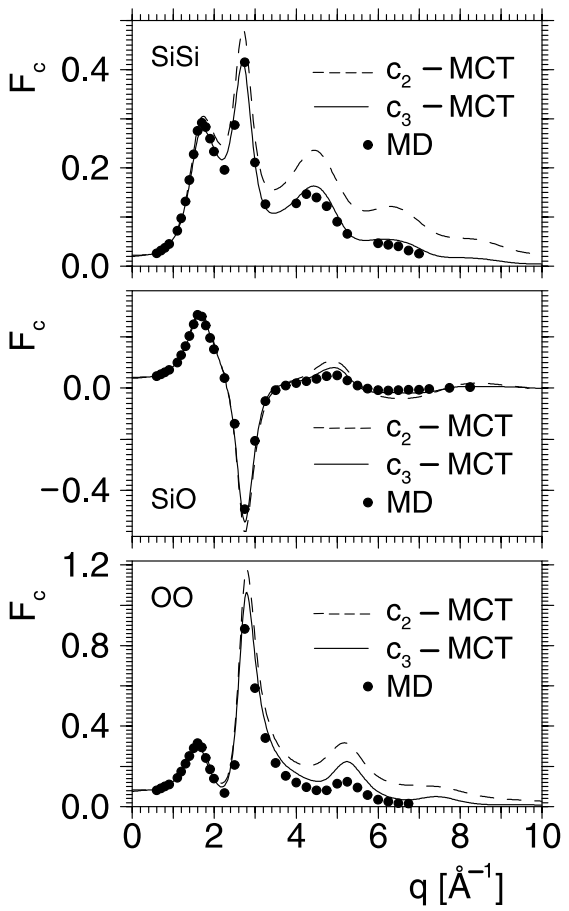

Fig. 5. Same as Fig. 4 but for the case of silica.

5. Summary

The goal of this work was to check to what extent the mode-coupling theory of the glass transition is able to give a correct *quantitative* description of the dynamics of glass-forming liquids. This was done for two very different types of systems: a binary mixture of Lennard-Jones particles, whose structure is similar to the one of a close packing of hard spheres and whose temperature dependence of relaxation times makes it a glass-forming liquid of intermediate fragility. On the other hand we have studied silica, which has a open network structure and which, in the temperature region where experiments are feasible, is considered to be the prototype of a strong glass former.

For the BMLJ system we have solved the MCT equations to obtain the full time and wave vector dependence of the relaxation dynamics. In particular we have also included a realistic Ansatz for the dynamics at short times so that the theoretical curves should be able to give also a good description in this time regime. By comparing the theoretical curves for $F(q,t)$ and $F_s(q,t)$ with the ones obtained from computer simulations of the same system, we find that cage effects become noticeable already at relatively high temperatures. The theory is able to give a very reliable quantitative description of the relaxation dynamics for all temperatures considered. The only discrepancy found is probably related to the fact that our understanding of the dynamics at *short* times is still incomplete.

For the case of silica we have calculated the q-dependence of the NEPs. We have found that for this system it is important to include in the evaluation of the memory function also those contributions that stem from three point correlation functions. Most probably this finding is related to the open network structure of the system. We find that once c_3 is taken into account the prediction of the theory for the NEP are in very good agreement with the results from computer simulations.

In summary we have shown that MCT is able to give a very good *quantitative* description of the relaxation dynamics of fragile as well as strong liquids, at least at high and intermediate temperatures. Thus we conclude that this theory is able to rationalize *at least* the first few decades of the slowing down of a very large class of glass-forming liquids on a quantitative level.

Acknowledgements

We thank L. Fabbian for contributing to the early development of this research, and W. Götze for useful discussions on this work. Part of this work was supported by the DFG through SFB 262. F.S. acknowledges support from INFM-PRA-HOP and MURST-PRIN2000. W.K. thanks the Universitá La Sapienza for a visiting professorship during which part of this work was carried out.

References

[1] See, e.g., Proceedings of Third International Discussion Meeting, J. Non-Cryst. Solids, Vols. 235–237 and Proceedings of Unifying Concepts in Glass Physics Trieste, September 1999; J. Phys.: Condens. Matter 12 (2000).
[2] W. Götze, J. Phys.: Condens. Matter 10 (1999) A1.
[3] J.-L. Barrat, A. Latz, J. Phys.: Condens. Matter 2 (1990) 4289.
[4] W. Götze, L. Sjögren, Phys. Rev. A 43 (1991) 5442.
[5] M. Fuchs, I. Hofacker, A. Latz, Phys. Rev. A 45 (1992) 898.
[6] M. Fuchs, W. Götze, S. Hildebrand, A. Latz, Z. Phys. B 87 (1992) 43.
[7] M. Nauroth, W. Kob, Phys. Rev. E 55 (1997) 657.
[8] L. Fabbian, A. Latz, R. Schilling, F. Sciortino, P. Tartaglia, C. Theis, Phys. Rev. E. 60 (1999) 5768;
C. Theis, F. Sciortino, A. Latz, R. Schilling, P. Tartaglia, Phys. Rev. E 62 (2000) 1856.
[9] A. Winkler, A. Latz, R. Schilling, C. Theis, Phys. Rev. E 62 (2000) 8004.
[10] M.H. Nauroth, PhD thesis, Technical University of Munich, 1999.
[11] F. Sciortino, W. Kob, Phys. Rev. Lett. 86 (2001) 648.
[12] K. Tankeshwar, K.N. Pathak, S. Ranganathan, J. Phys. C 20 (1987) 5749;
K. Tankeshwar, K.N. Pathak, S. Ranganathan, J. Phys.: Condens. Matter 7 (1995) 5729.
[13] J.P. Boon, S. Yip, Molecular Hydrodynamics, Dover, New York, 1980.
[14] W. Kob, H.C. Andersen, Phys. Rev. E 51 (1995) 4626;
W. Kob, H.C. Andersen, Phys. Rev. E 52 (1995) 4134.
[15] T. Gleim, W. Kob, K. Binder, Phys. Rev. Lett. 81 (1998) 4404;
T. Gleim, PhD thesis, Mainz University, 1999.
[16] W. Kob, J. Phys.: Condens. Matter 11 (1999) R85.
[17] B.W.H. van Beest, G.J. Kramer, R.A. van Santen, Phys. Rev. Lett. 64 (1990) 1955.
[18] J. Horbach, W. Kob, Phys. Rev. B 60 (1999) 3169.
[19] J. Horbach, W. Kob, Phys. Rev. E 64 (2001) 041503.
[20] I. Saika-Voivod, P.H. Poole, F. Sciortino, Nature 412 (2001) 514.
[21] W.H. Zachariasen, J. Am. Chem. Soc. 54 (1932) 3841.
[22] J.-L. Barrat, W. Götze, A. Latz, J. Phys.: Condens. Matter 1 (1989) 7163.