

# The $\beta$ -relaxation dynamics of a simple liquid

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Received 5 February 1999 and Received in final form 7 June 1999

**Abstract.** We present a detailed analysis of the  $\beta$ -relaxation dynamics of a simple glass former, a binary Lennard-Jones system with a stochastic dynamics. By testing the various predictions of mode-coupling theory, including the recently proposed corrections to the asymptotic scaling laws, we come to the conclusion that in this time regime the dynamics is described very well by this theory.

**PACS.** 61.20.Lc Time-dependent properties; relaxation – 61.20.Ja Computer simulation of liquid structure – 02.70.Ns Molecular dynamics and particle methods

## 1 Introduction

In the last few years it has been demonstrated that mode-coupling theory (MCT) [1] is able to describe many aspects of the relaxation dynamics of supercooled liquids. In particular the theory is able to explain on a qualitative level, and for certain systems even on a quantitative one, phenomena like the non-Debye behavior of the  $\alpha$ -relaxation process, the wave-vector dependence of the Lamb-Mössbauer and Debye-Waller factors, and why quantities like the viscosity or the  $\alpha$ -relaxation times show an anomalously strong temperature dependence of their activation energy in the vicinity of  $T_c$ , the so-called critical temperature in the theory.

Apart from the existence of  $T_c$ , the most important predictions of MCT deal with the so-called  $\beta$ -relaxation process which is proposed to exist in the supercooled regime on the time scale between the microscopic relaxation at short times and the  $\alpha$ -relaxation at long times. The  $\beta$ -regime is readily seen if a time correlation function  $\phi(t)$ , such as the intermediate scattering function, is plotted *versus* the logarithm of time. In the supercooled regime  $\phi(t)$  will show at intermediate times a plateau, and the relaxation dynamics of the system on the time scale at which  $\phi(t)$  is close to this plateau is the  $\beta$ -regime. The reason for the existence of this plateau is that on this time scale the particles are trapped in the cages formed by their surrounding neighbors. Hence the predictions of the theory regarding the  $\beta$ -regime deal with the details of the dynamics of the particles in these cages. Some of these predictions have already been confirmed by various experiments on colloidal suspensions and molecular liquids [2].

In the past it has been shown that apart from experiments also computer simulations are a very useful tool to probe the dynamics of supercooled liquids [3]. Be-

cause simulations allow the investigations of observables which in real experiments are hard to measure, as *e.g.* the dynamics at large wave-vectors or cross-correlation functions, they permit to make more stringent tests of theoretical concepts and thus are a valuable addition to experiments. Results of such tests have, *e.g.*, been done for soft sphere systems [4], Lennard-Jones models [5], water [6], and polymers [7]. The result of these tests was that the theory is indeed able to give a good description of the relaxation dynamics of these systems. What these simulations have, however, not been able to address so far are several important predictions, discussed below, of MCT about the relaxation dynamics in the  $\beta$ -regime. The main reason why these predictions have not been tested was that they are supposed to be valid only very close to the critical temperature  $T_c$  of MCT, and that close to  $T_c$  the relaxation times of the system are usually so large that it is very hard to equilibrate the system within the time span accessible to a computer simulation (but easily reachable in a real experiment). If the predictions of the theory are tested at slightly higher temperatures, where the system can be equilibrated even in a computer simulation, the strong interference of the microscopic dynamics of the system with the  $\beta$ -relaxation process will spoil the analysis, because of the lack of separation of time scales, and stringent tests will almost be impossible. In order to overcome these problems we have recently investigated the relaxation dynamics of a Lennard-Jones system in which the particles move according to a stochastic dynamics [8]. This dynamics leads to a strong damping of the microscopic dynamics and hence it becomes finally possible to test the predictions of MCT about the  $\beta$ -regime and in this paper we report the outcome of these tests.

The model we investigate is a 80:20 mixture of Lennard-Jones particles with mass  $m$ . In the following we will call the two species of particles A and B. The interaction between two particles of type  $\alpha$  and  $\beta$ ,

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with  $\alpha, \beta \in \{A, B\}$ , is given by  $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$  with  $\epsilon_{AA} = 1.0$ ,  $\sigma_{AA} = 1.0$ ,  $\epsilon_{AB} = 1.5$ ,  $\sigma_{AB} = 0.8$ ,  $\epsilon_{BB} = 0.5$ , and  $\sigma_{BB} = 0.88$ , and a cut-off radius of  $2.5\sigma_{\alpha\beta}$ . In the following we will always use reduced units with  $\sigma_{AA}$  and  $\epsilon_{AA}$  the unit of length and energy, respectively (setting the Boltzmann constant  $k_B$  equal to 1.0). Time is measured in units of  $\sqrt{\sigma_{AA}^2 m/48\epsilon_{AA}}$ . The volume of the simulation box is kept constant with a box length of 9.4. The dynamics of the system is given by the stochastic equations of motion

$$m\ddot{\mathbf{r}}_j + \nabla_j \sum_l V_{\alpha_j\beta_l}(|\mathbf{r}_l - \mathbf{r}_j|) = -\zeta\dot{\mathbf{r}}_j + \eta_j(t). \quad (1)$$

Here  $\eta_j(t)$  is a Gaussian distributed white noise force with zero mean. Because of the fluctuation dissipation theorem, the magnitude of  $\eta_j(t)$  is related to  $\zeta$  by  $\langle \eta_j(t) \cdot \eta_l(t') \rangle = 6k_B T \zeta \delta(t - t') \delta_{jl}$ . We have used a value of  $\zeta = 10$ , which is so large that the presented results for the dynamics do not depend on  $\zeta$  anymore (apart from a trivial change of the time scale). Equations (1) were solved with a Heun algorithm with a time step of 0.008. The temperatures investigated were 5.0, 4.0, 3.0, 2.0, 1.0, 0.8, 0.6, 0.55, 0.5, 0.475, 0.466, 0.452, and 0.446. At the lowest temperature the length of the run was  $4 \times 10^7$  time steps. This length is not sufficiently long to equilibrate the sample. Therefore we equilibrated the system by means of a Newtonian dynamics for which we have found that the equilibration times are significantly shorter [8]. Thus all the correlation functions shown in the present work are equilibrium curves, even if they do not decay to zero at long times. In order to improve the statistics of the results we averaged at each temperature over eight independent runs.

In the following we will review some of the predictions of MCT about the dynamics in the  $\beta$ -regime and will denote by  $\phi_l(t)$  an arbitrary time correlation function which couples to density fluctuations. (Here the index  $l$  is just used to distinguish between different correlators.) As stated here, the predictions are valid only for temperatures slightly *above* the critical temperature  $T_c$  of MCT. More general results can be found in references [1, 9].

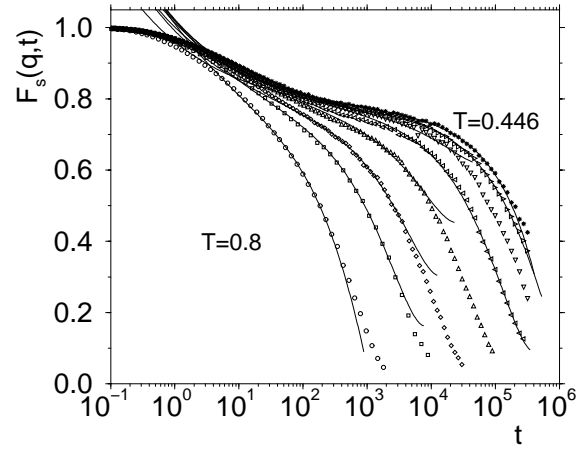
MCT predicts that in the  $\beta$ -region any correlation function  $\phi_l(t)$  can be written as

$$\phi_l(t) = f_l^c + h_l c_\sigma g_-(t/t_\sigma), \quad (2)$$

where the temperature independent constants  $f_l^c$  and  $h_l$  are called critical nonergodicity parameter and critical amplitude, respectively. The quantity  $c_\sigma$  is given by

$$c_\sigma = \sqrt{|\sigma|} \quad \text{with} \quad \sigma = C(T_c - T), \quad (3)$$

where  $C$  is a constant. The function  $g_-$  is independent of  $\phi_l$  and depends only on the so-called ‘‘exponent parameter’’  $\lambda$  which can be calculated from the structure factor [1]. This calculation has been done for the present system and a value of  $\lambda = 0.708$  was found [10]. Hence in our case  $\lambda$  is not a fit parameter. Once  $\lambda$  is known, the function  $g_-$  can be calculated numerically.



**Fig. 1.** Time dependence of  $F_s(q, t)$  for the A particles at  $q = 7.2$  (symbols) and the fitted  $\beta$ -correlators (solid curves) for all  $T \leq 0.8$ .

The quantity  $t_\sigma$  in equation (2) is the time scale of the  $\beta$ -relaxation and is given by

$$t_\sigma = t_0/|\sigma|^{1/2a}, \quad (4)$$

where  $t_0$  is a system universal constant, and the exponent  $a$  can be calculated from  $\lambda$  and is in our case  $a = 0.324$  [10]. Hence, according to MCT, in equation (2) only the time scale  $t_\sigma$  and the prefactor  $h_l c_\sigma$  depend on temperature.

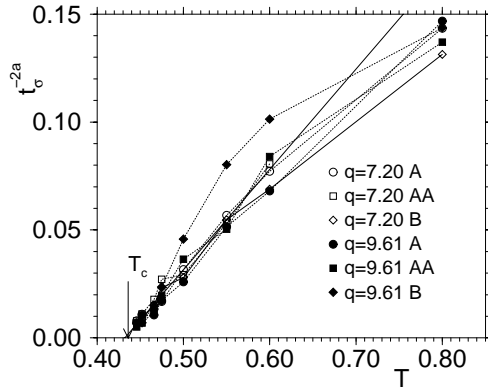
MCT also predicts that  $\tau_l(T)$ , the time scale of the  $\alpha$ -relaxation, depends on temperature like

$$\tau_l = \Gamma_l \tau, \quad \tau = t_0/|\sigma|^\gamma, \quad \text{with} \quad \gamma = 1/2a + 1/2b \quad (5)$$

where  $\Gamma_l$  is independent of temperature and the exponent  $b$  can also be calculated from  $\lambda$  [1] and is for our system  $b = 0.627$  [10]. Thus we have  $\gamma = 2.34$ .

Having presented some of the predictions of MCT about the  $\beta$ -relaxation we can now check how well they agree with reality. For this we calculated from the simulation  $F^{\alpha\beta}(q, t)$  and  $F_s^\alpha(q, t)$ , the coherent and incoherent scattering functions for wave-vector  $q$ , respectively. These time correlation functions were then fitted in the  $\beta$ -relaxation regime with the functional form given by equation (2), where  $f_l^c$ ,  $h_l c_\sigma$ , and  $t_\sigma$  were fit parameters. This fit was first done for the lowest temperature ( $T = 0.446$ ). For the fits at the higher temperatures the value of  $f_l^c$  was kept fixed to the one of  $T = 0.446$  in order to avoid that the fits give some *effective* time scales  $t_\sigma$  and prefactors  $h_l c_\sigma$ . In Figure 1 we show the results of such fits and it can be seen that the range over which the  $\beta$ -correlator describes the data increases with decreasing temperature, as predicted by MCT. (Note that in order to obtain reliable values of the fit parameters  $f_l^c$  it was necessary to include also the next order correction to  $g_-(t/t_\sigma)$  which is of the form of  $(t/\tau_l)^{(2b)}$  [1, 6]. These corrections give rise to the slight upward bending of the fits at long times.)

From equations (3, 4) it follows that according to MCT a plot of  $t_\sigma^{-2a}$  versus temperature should give a straight



**Fig. 2.** Check of the validity of equation (4) for various correlators (see labels of curves). MCT predicts a straight line which intercept the  $T$ -axis at  $T_c = 0.435$ . The bold straight line is a linear fit to the open circles.

line and that this line should be independent of the correlator  $\phi_l$ . In Figure 2 we show such a plot where we have used for  $\phi_l$  the functions  $F_s^\alpha(q, t)$  for the A and B particles and the function  $F^{AA}(q, t)$ , for two wave-vectors:  $q = 7.20$  and  $q = 9.61$ , which correspond to the location of the maximum and first minimum in the structure factor for the A-A correlation [5]. From this plot we see that at low temperatures the different curves are indeed close to straight lines and collapse quite well onto a master curve. Hence we conclude that these two predictions of MCT work well for our system. Also included in the figure is a linear fit to the data for  $F_s^A(q, t)$  for  $q = 7.2$ . This fit intercepts the temperature axis at  $T \approx 0.432$ , which according to MCT should be  $T_c$ . This estimate of the critical temperature is in excellent agreement with the one of reference [5], where  $T_c = 0.435$  was found.

We also mention that we have found that the square of the prefactor in equation (2),  $h_l c_\sigma$ , shows a linear dependence on  $T$ ,  $(h_l c_\sigma)^2 = |\sigma|$ , and vanishes at  $T_c$ , which follows from equations (2, 3) and is hence in agreement with MCT. The test of equation (3) is equivalent to the test of the relation between  $h_l c_\sigma$  and  $t_\sigma$ , which according to the theory, equations (2, 3, 4), should be

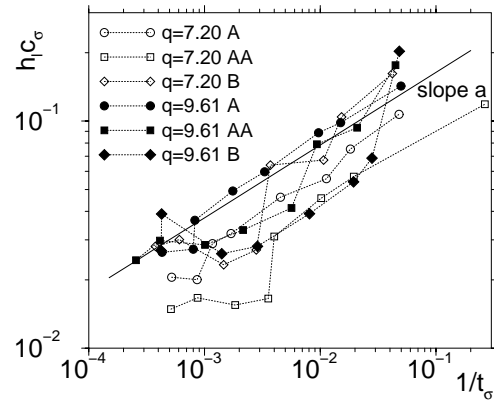
$$h_l c_\sigma \propto t_\sigma^{-a}. \quad (6)$$

In Figure 3 we plot  $h_l c_\sigma$  versus  $1/t_\sigma$  in a double logarithmic plot for the same correlators discussed in Figure 2. We see that the different curves can be approximated reasonably well by straight lines with a slope  $a$  (bold solid line in the figure). Therefore we conclude that also this prediction of the theory seems to work satisfactorily well.

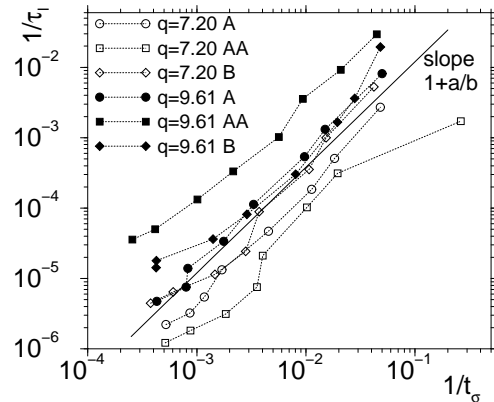
From equations (4, 5) it follows that also the  $\alpha$ -relaxation time  $\tau_l$  should show a power-law dependence on  $t_\sigma$ , *i.e.*

$$\tau_l \propto \Gamma_l t_\sigma^{1+a/b}. \quad (7)$$

Thus this equation expresses the surprising prediction of MCT that *two* diverging time scales exist in supercooled liquids, namely  $\tau_l$  and  $t_\sigma$ . Whether this is indeed the case is tested in Figure 4 where we plot  $\tau_l^{-1}$  versus  $t_\sigma^{-1}$  for the



**Fig. 3.** Check of the validity of equation (6) for various correlators. The prediction of MCT is a straight line with slope  $a$  (bold straight line).



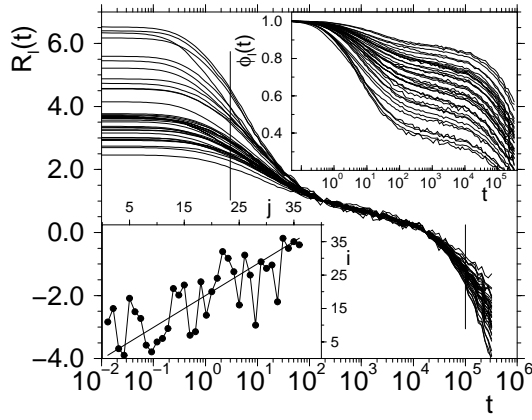
**Fig. 4.** Check of the validity of equation (7) for various correlators. The prediction of MCT is a straight line with slope  $1 + a/b$  (bold straight line).

usual correlators in a double logarithmic plot. We see that the different curves are indeed close to straight lines and that the slope is very close to the theoretical value, bold straight line. Thus we confirm also this prediction of the theory.

As already mentioned above in the context of equation (2), according to MCT the whole time dependence of  $\phi_l(t)$  is given by the  $l$ -independent function  $g_-(t/t_\sigma)$ . In order to test this prediction we can introduce a function  $R_l(t)$  as follows:

$$R_l(t) = \frac{\phi_l(t) - \phi_l(t')}{\phi_l(t'') - \phi_l(t')}. \quad (8)$$

Here  $t'$  and  $t''$  are arbitrary times in the  $\beta$ -relaxation regime ( $t' \neq t''$ ). From equation (2) it follows immediately that in the  $\beta$ -regime the function  $R_l(t)$  is independent of the correlator, *i.e.* of  $l$ . To see whether this is indeed the case we have considered the correlation function discussed in the context of Figure 2 and in addition the coherent and incoherent scattering function for several other wave vectors and also the cross correlation function  $F^{AB}(q, t)$  at different  $q$ . This gave us a total of 36 correlation functions which are shown in the upper inset of Figure 5 (at  $T = 0.446$ ). For each of these functions we determined the corresponding  $R_l(t)$ , choosing for  $t'$  and  $t''$  a value around



**Fig. 5.** Main figure: Time dependence of the ratio given in equation (8), demonstrating the validity of the factorization property (Eq. (2)).  $T = 0.446$ . The correlation functions  $\phi_l(t)$  are shown in the upper right inset. See text for the discussion of the lower left inset and the two vertical lines in the main figure.

200 and 15000, respectively. In the main figure of Figure 5 we show the different  $R_l(t)$  and we see that in the  $\beta$ -regime they do indeed collapse onto a master curve. That such a collapse is not a trivial result can be concluded from the observation that outside the  $\beta$ -regime the different curves show a strong dependence on  $l$ , at short as well as at long times.

Equation (2) is the prediction of the theory about the *leading* asymptotic behavior for the time and temperature dependence of a generic correlator. Very recently the next order corrections to this behavior have been calculated [11] and these corrections can now be used to do more checks on the validity of the theory. In reference [11] it has been shown that in the *early*  $\beta$ -relaxation regime, *i.e.* for  $t_0 \ll t \ll t_\sigma$ , the correlator can be written as

$$\phi_l(t) = f_l^c + h_l(t_0/t)^a \{1 + [K_l + \Delta](t_0/t)^a\}. \quad (9)$$

Here  $\Delta$  is a  $l$ -independent constant and the constant  $K_l$  depends on  $l$  but not on temperature. In the *late*  $\beta$ -regime, for which  $t_\sigma \ll t \ll \tau_l$ , the correlation function is predicted to behave like

$$\phi_l(t) = f_l^c - h_l(t/\tau)^b \{1 - K_l(t/\tau)^b\}. \quad (10)$$

The mentioned corrections are the second terms in the curly brackets in equations (9, 10). The important result about these equations is that the  $l$  dependent part of the correction, *i.e.*  $K_l$ , is the same. Using this fact it is simple to show the following: Calculate the ratio  $R_l(t)$  from equation (8) for various correlators and plot these  $R_l(t)$  versus the logarithm of  $t$ . Draw two vertical lines at times that are a bit shorter and a bit longer than the times where the asymptotic expression, equation (2), holds. Start to label the correlators from top to bottom in the order they intersect the vertical line at *short* times and call this number  $i$ . Determine the position  $j$  at which curve  $i$  intersects the vertical line at *large* times, where the counting is again done from top to bottom. Thus this gives a function  $j(i)$ . From equations (9, 10) it then follows that  $j = i$ . Or to

put this in other words: the first (second, ...) curve that intersects the left vertical line is also the first (second, ...) curve to intersect the right vertical line.

We have done the described procedure by using vertical lines at  $t = 3$  and  $t = 10^5$  (bold vertical lines in Fig. 5). The function  $j(i)$  we find is shown in the lower inset of Figure 5. We see that, despite the scattering present in the data, a clear increasing trend which is compatible with a straight line with unit slope can be seen, thus giving also support for the validity of this prediction of the theory.

We thus can conclude from the present work that many of the predictions that mode-coupling theory makes for the  $\beta$ -relaxation can also be tested in computer simulations. As we have shown in this paper the outcome of such tests for the Lennard-Jones system considered here is that the theory is indeed able to give a self consistent picture of the dynamics of this simple glass-former in the  $\beta$ -relaxation regime.

We thank W. Götze and A. Latz for valuable discussions and comments on a draft of this paper. Part of this work was supported by the DFG under SFB 262/D1.

## References

1. W. Götze, L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992); W. Kob, in *Experimental and Theoretical Approaches to Supercooled Liquids: Advances and Novel Applications*, edited by J. Fourkas, D. Kivelson, U. Mohanty, K. Nelson (ACS Books, Washington, 1997) p. 28; W. Götze, J. Phys. Cond. Matter **11**, A1 (1999).
2. See, *e.g.*, *Proceedings of Second and Third International Discussion Meetings*, J. Non-Cryst. Solids **172-174** (1994) and **235-237** (1998).
3. See, *e.g.*, W. Kob, J. Phys. Cond. Matter **11**, R85 (1999), and references therein.
4. J.N. Roux, J.-L. Barrat, J.-P. Hansen, J. Phys. Cond. Matter **1**, 7171 (1989).
5. W. Kob, H.C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994); Phys. Rev. E **51**, 4626 (1995); *ibid.* **52**, 4134 (1995).
6. P. Gallo, F. Sciortino, P. Tartaglia, S.-H. Chen, Phys. Rev. Lett. **76**, 2730 (1996); F. Sciortino, P. Gallo, P. Tartaglia, S.-H. Chen, Phys. Rev. E **54**, 6331 (1996); F. Sciortino, L. Fabbian, S.-H. Chen, P. Tartaglia, *ibid.* **56**, 5397 (1997).
7. J. Baschnagel, Phys. Rev. B **49**, 135 (1994); J. Baschnagel, M. Fuchs, J. Phys. Cond. Matter **7**, 6761 (1995); C. Bennemann, W. Paul, K. Binder, B. Dünweg, Phys. Rev. E **57**, 843 (1998); C. Bennemann, J. Baschnagel, W. Paul, Eur. Phys. J. B **10**, 323 (1999).
8. T. Gleim, W. Kob, K. Binder, Phys. Rev. Lett. **81**, 4404 (1998); T. Gleim, PhD thesis (Mainz University, 1999).
9. W. Götze, Z. Phys. B **60**, 195 (1985); W. Götze, L. Sjögren, J. Phys. Cond. Matter **1**, 4183 (1989); M. Fuchs, W. Götze, S. Hildebrand, A. Latz, Z. Phys. B **87**, 43 (1992); M. Fuchs, W. Götze, S. Hildebrand, A. Latz, J. Phys. Cond. Matter **4**, 7709 (1992).
10. M. Nauroth, W. Kob, Phys. Rev. E **55**, 657 (1997).
11. T. Franosch, M. Fuchs, W. Götze, M.R. Mayr, A.P. Singh, Phys. Rev. E **55**, 7153 (1997); M. Fuchs, W. Götze, M.R. Mayr, Phys. Rev. E **58**, 3384 (1998).