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# On the mode-coupling-theory $\beta$-correlator

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**Abstract.** We examine the possibility of detecting mode-coupling $\beta$-correlator behaviour in the time dependence of correlation functions of supercooled liquids. We compare the theoretical scaling predictions with several translational and rotational correlation functions calculated from molecular dynamics trajectories as well as with correlation functions evaluated by solving the mode-coupling equations for hard spheres. We find that while the ideal glass transition point can be unambiguously determined by studying the evolution of correlators on approaching the glass point, the *pure* $\beta$-correlator dynamics is hardly measurable. Information on the $\alpha$-scaling is important for a proper determination of the MCT critical exponents.

## 1. Introduction

Mode-coupling theory (MCT) for supercooled liquids [1, 2] predicts that close to the ideal MCT glass transition, i.e. when asymptotic predictions became relevant, the time dependence of all of the correlation functions $\phi(t)$ which couple to the density is described by a well defined function $g_\lambda$, where the exponent parameter $0.5 \leqslant \lambda \leqslant 1$ depends on the liquid structure at the ideal glass transition point. This prediction is valid in the so-called $\beta$-region, i.e. the time window in which the values of the correlation functions are close to their non-ergodicity parameter $f_c$. Of course, the external control parameters (for example, pressure and density) must be close to their critical values. In the $\beta$-region, all functions $\phi(t)$ are predicted to follow the law

$$\phi(t) = f_c + h g_\lambda(t/t_\sigma) \tag{1}$$

where the correlator-dependent critical amplitude $h$ and the correlator-independent timescale $t_\sigma$ depend on the relative distance from the ideal glass transition point $\epsilon$ as follows:

$$h \sim \epsilon^{1/2} \qquad t_\sigma \sim \epsilon^{-1/2a}. \tag{2}$$

The critical exponent $a$ is fixed by the value of $\lambda$.

Recently, the next-to-leading-order expansion of the critical decay has been worked out [3]. Corrections to scaling have an intensity which is strongly correlator dependent and which may completely mask the leading-order behaviour. A complete MCT solution is required to predict which correlators are less affected by second-order correction and are thus good candidates for showing the universal pattern at finite distance from the critical point.

Two further complications hide the asymptotic result of equation (1). On the short-time side, the timescale of the microscopic dynamics often extends in time and overlaps with the critical behaviour. Sound waves, hindered rotational and translational motions, and bending modes may give rise to slow microscopic processes. On the long-time side, decorrelation

  

channels not included in the ideal MCT theory become more and more relevant on approaching the critical temperature. In systems where hopping effects are relevant, the $\beta$-correlator decay can be confined for a narrow range of control parameters, limited from above by the requirement of validity of the asymptotic solutions and from below by the requirement that the leading decay channels are still the ones included in the ideal version of the MCT. Predictions for the decay of correlation in presence of hopping in the $\beta$-region can be formulated in the extended version of the MCT theory [1] (and have been compared with experimental [4, 5] and simulation results [6]). Still, at the present time only the leading corrections are known and in our opinion this is not sufficient to disentangle the contribution from hopping from the (correlator-dependent) contribution of the next-to-leading-order corrections.

In this article we critically discuss the possibility of describing unambiguously the decay of correlations in the $\beta$-region using *only* equation (1). We emphasize the word *only* since it has been proved [7, 8] that MCT is able to describe successfully the slow dynamics in supercooled liquids once information on the $\alpha$-relaxation scaling is taken into account together with the $\beta$-correlator next-to-leading-order corrections. We aim to show that only if hopping effects are negligible at a relative distance $\epsilon \leqslant 10^{-3}$ can a procedure of fitting to several correlation functions be used to determine the value of $\lambda$. When systems with $\epsilon \geqslant 10^{-3}$ are studied, the uncertainties on the values of the non-ergodicity parameters and on the amplitude of the next-to-leading-order corrections, as well as the non-negligible role of the microscopic dynamics, may prevent a proper determination of $\lambda$. In this last case, information on the temperature or density dependence of the $\alpha$-relaxation time may provide a way of reducing the error in the estimate of $\lambda$.

In this article we analyse two sets of correlation functions. One is based on translational and rotational correlators evaluated from a molecular dynamics simulation of a large system of three-site molecules interacting with the Lewis and Wahnström potential [9], originally designed to mimic the behaviour of orthoterphenyl. The other set is composed by self-density [10] and collective density [3] correlators obtained by solving the $q$-dependent ideal MCT equations for the hard-sphere liquid (using the Percus–Yevick approximation for the input structure factor). We will show fits of the two sets of correlation functions made assuming two well separated values of $\lambda$, i.e. $\lambda = 0.55$ and $\lambda = 0.70$.

## 2. Correlation functions

We have performed molecular dynamics simulations of 9261 molecules in a cubic box interacting via the Lewis and Wahnström potential [9], i.e. a rigid three-site model in which sites interact with a Lennard-Jones potential. We have simulated the same state points as in reference [9], but for times up to 50 ns. The large size of the simulated system eliminates spurious oscillations appearing in correlation functions at short time, connected to the low-frequency cut-off of the density of states imposed by the boundary conditions and/or by the undamped propagation of the sound waves, through the boundary conditions [11]. From the trajectory of the system in configuration space, we have calculated the coherent and incoherent correlation functions, for both sites and the centre of mass, as well as the Legendre polynomials for the principal axis of symmetry of the molecule. This ensemble of correlation functions constitutes the set labelled LW.

The second set of correlation functions is composed of by four collective and four self-normalized intermediate-scattering functions for the hard-sphere (HS) liquid. The corresponding $q$-vectors (in units of $\sigma$, the hard-sphere diameter) are $q_0 = 3.4$, $q_1 = 7.0$ (the structure factor peak), $q_2 = 10.6$, and $q_3 = 17.4$. The correlation functions are solutions of the MCT equations discretized on a grid of 100 $q$-vectors at three different packing fractions, cor-

responding to relative distances from the critical packing fraction of $2.15\times10^{-3}$, $1.0\times10^{-2}$, and $4.6\times10^{-2}$. A full description of this model can be found in references [3,10]. The three packing fractions studied here correspond to $n = 4$, 6, and 8 in the notation of references [3, 10]. For our purpose, we recall that a Brownian dynamics has been considered to model the microscopic dynamics, that the theoretical value of the exponent parameter is $\lambda = 0.735$, and that the $f_c(q)$ are also known.

## 3. The fitting procedure

In the present discussion we fix $\lambda = 0.55$ (corresponding to $a = 0.38$) or $\lambda = 0.70$ (corresponding to $a = 0.33$). If the asymptotic prediction of equation (1) holds, once $\lambda$ is fixed, fixing the non-ergodicity parameter of one arbitrary correlator, at one fixed distance from the critical point, completely defines $t_\sigma$ and as a consequence the non-ergodicity parameters of all other correlators. Indeed, since we know the time at which

$$\phi(t) = f_c \tag{3}$$

then by solving

$$g_\lambda(t/t_\sigma) = 0 \tag{4}$$

we can calculate the correlator-independent value of $t_\sigma$. In other words, in the truly asymptotic region, all correlators cross their $f_c$-value at the same time. Since the $f_c$-values are not temperature (or density) dependent, the temperature (or density) dependence of $t_\sigma$ is also determined. We stress that without using any fitting procedure, by arbitrarily fixing the value of the non-ergodicity parameter for one arbitrary correlator, it is possible to check equation (1) by calculating the $t_\sigma$ versus $\epsilon^{-2a}$ dependence for several correlators.

Selection of an $\epsilon$-dependent fitting interval is the obvious choice. Finally, a simple fitting procedure allows the evaluation of $h$. In principle, the $\epsilon$-dependence of $h$ and $t_\sigma$ can be used to strengthen the validity of the assumed values for $\lambda$ and $f_c$.

In the case of the HS set, we will compare three cases:

- $\lambda = 0.70$, $f_c$ constrained to the theoretical values;
- $\lambda = 0.55$, $f_c$ constrained to the theoretical values;
- $\lambda = 0.55$, with arbitrary $f_c$.

In the case of the LW set, we will compare the two cases:

- $\lambda = 0.70$, for three different values of $f_c$;
- $\lambda = 0.55$, for the same three different values of $f_c$.

## 4. Discussion

Indications of the possibility of detecting the $\beta$-correlator can be obtained without using any fitting procedure, by comparing—for several correlators—the susceptibility spectra for the smallest $\epsilon$. Indeed, in the $\beta$-region, sufficiently close to the ideal glass transition, all spectra should show minima at the same position. Figure 1 (left) shows the susceptibility spectra for several correlators at $T = 266$ K, close to the estimated glass transition temperature for the LW potential (i.e. $\Delta T/T_c \leqslant 0.02$). Figure 1 (right) shows similar quantities for the HS system for $\epsilon = 2.15 \times 10^{-3}$. In both systems, the frequencies $\omega_{min}$ at which $\chi''$ is at a minimum are spread around one decade, *apparently* violating the asymptotic predictions of equation (1). On the other hand, in the HS case, by construction, the susceptibility spectra are the theoretical

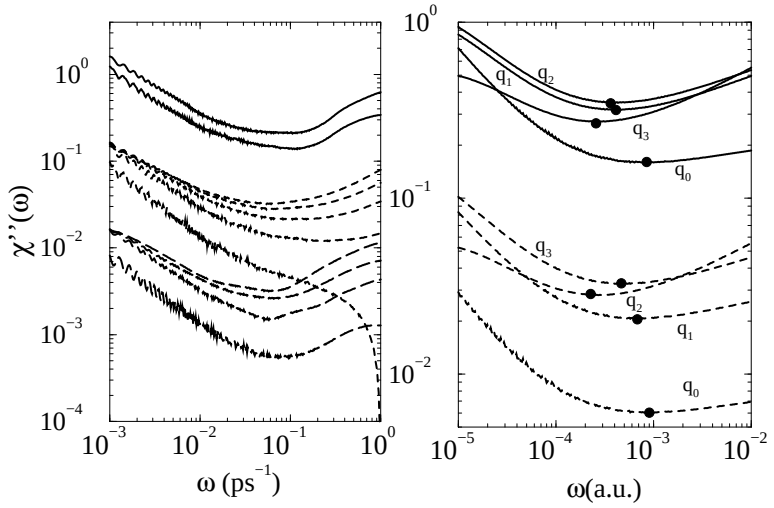


**Figure 1.** Susceptibility spectra $\chi(\omega)$ for the LW (left) and the HS (right) sets. Left: from top to bottom: centre-of-mass self-correlators at $q = q_{min}$ and $q = q_{max}$, where $q_{max}$ and $q_{min}$ indicate the positions of the first maximum and minimum of the structure factor; the first five Legendre polynomials for the principal symmetry axis; and the collective density correlators for four different $q$-vectors. Self- and collective correlators have been shifted up or down by one decade for clarity. Right: self-correlators (dashed curves) and collective correlators (full curves). Collective correlators have been shifted up one decade for clarity.

MCT spectra. Thus, the data in figure 1 (right) prove that even when $\epsilon$ is of the order of $10^{-3}$, the asymptotic MCT predictions *alone* are not sufficient to describe the system's dynamics in the $\beta$-region for all correlators. Next-to-leading-order corrections play a fundamental role in the interpretation of the frequency dependence close to the susceptibility minimum, even close to the ideal glass transition.

When only one correlation function can be observed, a test for the presence of asymptotic behaviour can be made (and this has often been done in the past in the analysis of experimental data [12–14]) by studying the relation between $\omega_{min}$ and $\chi''_{min}$, which is predicted to be of the form

$$\chi''_{min} \sim \omega^a_{min}. \tag{5}$$

This test is one of the most convincing, since it does not require an *a priori* knowledge of the critical parameters. The only fitting parameters are the exponent $a$ and the amplitude of the power law. Log–log plots of $\chi''(\omega)$ versus $\omega$ at several temperatures for the LW case and at several densities for the HS case are shown in figure 2 together with the $\omega^a$-law. We note that in the LW case no clear $\omega^a$-law is observed, while in the HS case the $\omega^a$-dependence starts to be exhibited only when $\epsilon \leqslant 10^{-2}$. These data suggest that when hopping effects are absent and when no microscopic slow motions (such as undamped oscillations and rotations) are present, a relative distance of $10^{-2}$ could be sufficient for one to observe the behaviour described by equation (5).

We now turn to the analysis in the time domain. The analysis of the susceptibility in the $\omega$-domain requires fewer fitting parameters than the analysis of the correlation functions with respect to time, because the time-derivative operation implicit in the susceptibility eliminates the dependence on the value of the non-ergodicity parameter. The price to be paid is that, due to the different weights of the next-to-leading-order corrections, the range of validity

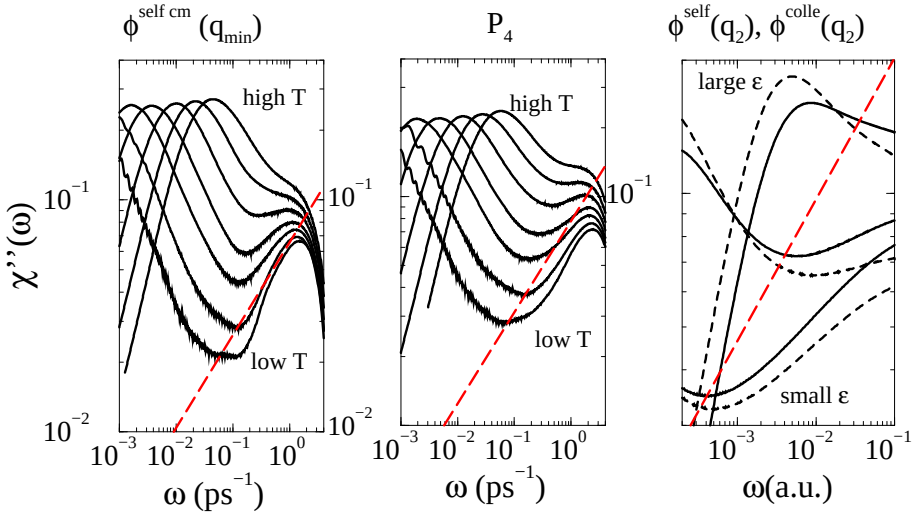


**Figure 2.** $\chi(\omega)$ for a few selected correlators for the LW (left and centre, respectively: centre-of-mass self-correlators and the fourth Legendre polynomial) and HS (right: both self- and collective correlators) cases. The temperatures vary from 266 K to 346 K for the LW case while $\epsilon$ is equal to $2.15 \times 10^{-3}$, $1.0 \times 10^{-2}$, $4.6 \times 10^{-2}$ for the HS case. The straight line represents, in the left and centre panels, $\omega^{0.4}$, the largest $\omega$-value consistent with MCT, while for the HS case it represents the theoretical asymptotic value $\omega^{0.32}$.

of the asymptotic predictions shrinks on going from the time to the frequency domain, as demonstrated in reference [3]. For this reason, evidence of a $\beta$-scaling could be observed in the time domain even if it is masked in frequency space. In the following we will compare the fittings of the correlation functions in the $\beta$-region, by arbitrarily fixing the value of $\lambda$ at 0.55 and 0.7. The study of the $\epsilon$-dependence of the parameters as well as the comparison with the exact MCT predictions for the HS case will be used to discuss the quality of the fit and to assess with what uncertainty it is possible to determine the value of the exponent parameter $\lambda$. Again we proceed by comparing the HS case and the LW case.

Figure 3 shows the best fit obtained for the HS case for the three cases studied, i.e. for the theoretical $\lambda = 0.7$ and $f_c$, for $\lambda = 0.55$ and theoretical $f_c$-values, and for $\lambda = 0.55$ and arbitrary $f_c$. The chosen $f_c$-values are shown in figure 3. We note that for the smallest $\epsilon$ the best fit to the data coincides with the theoretical predictions. When $\epsilon$ is $10^{-2}$ or more, a wrong choice of the non-ergodicity factors can partially compensate for the wrong choice of $\lambda$. We next study the $\epsilon$-dependence of the fitting parameter $h$ and $t_\sigma$. MCT predicts that $h^2$ varies linearly with the distance from the ideal glass transition point. Figure 4 shows $h^2$ for all three fitting cases from the simultaneous fit of all HS correlators. We note that the relation $h^2 \sim \epsilon$ is fulfilled in all cases, and thus it is not possible to discriminate between the correct case—in which the theoretical values for $f_c$ and for $\lambda$ are used—and the two wrong ones.

Fits of two rotational correlation functions for the LW case are shown in figure 5. In this case, we compare the two different choices of $\lambda$ with three different choices for $f_c$ (corresponding to three different values of $t_\sigma$). It is evident that different correlators would suggest different choices for $\lambda$ and $f_c$, again illustrating very clearly the need for an extended type of analysis including the correction to scaling.

The temperature dependence of the fitting parameters is reported for several different

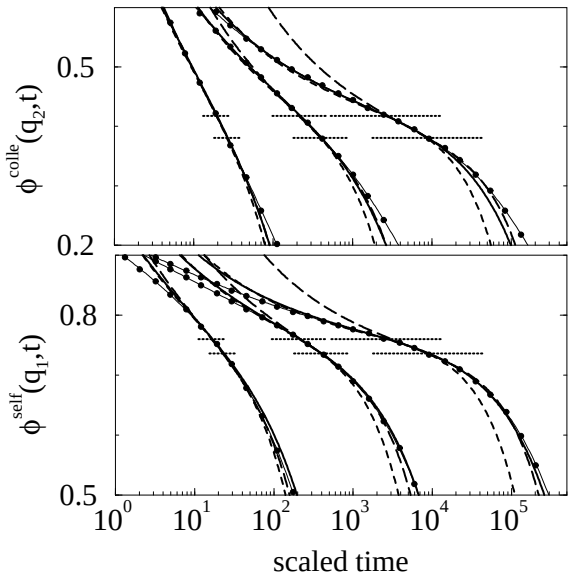


**Figure 3.** The best fit of two HS correlators for the three different relative distances $\epsilon$ from the ideal glass transition point. Each panel describes a different correlation function. The MCT correlators (full circles) are compared with the best fit obtained by fixing the exact $\lambda$ and the exact non-ergodicity factors (full curve), or by making the wrong choice of $\lambda = 0.55$ but with the theoretical ergodicity factors (short-dashed curve) or by making the wrong choice of $\lambda = 0.55$ and of the non-ergodicity factors (long-dashed curve). The fitting range—in time—is indicated by the short horizontal dashed lines.

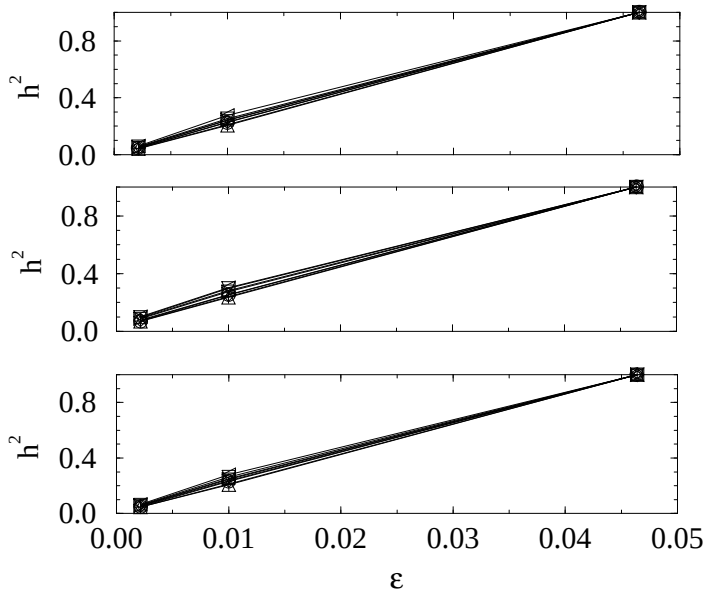


**Figure 4.** The $\epsilon$-dependence of the (scaled) fitting parameter $h^2$ for the three cases studied. Top: $\lambda = 0.55$; centre: $\lambda = 0.55$, $f_c$ wrong; bottom: $\lambda = 0.55$, theoretical $f_c$-values). The eight different symbols refer to the eight correlators studied. The data have been scaled according to the value of $h^2$ at the largest $\epsilon$.

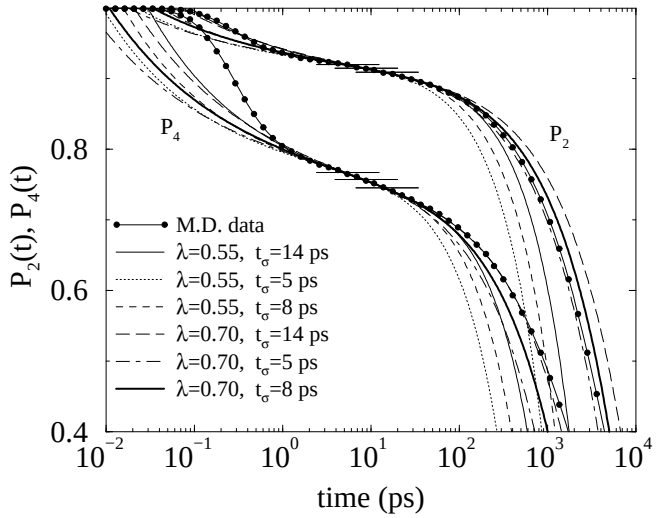


**Figure 5.** The second ($P_2$) and fourth ($P_4$) Legendre polynomials for the LW case at $T = 266$ K. Full circles indicate the molecular dynamics data; curves indicate the six different fits, labelled in the figure. The fitting range—of time—is indicated by the short horizontal lines.

correlators in figure 6. Consistently with the finding presented in figure 4, the $T$-dependence of $h^2$ is not sufficient to validate one set of fitting parameters and invalidate the others. The $t^{-1/2a}$-dependence of the scaling time as a function of temperature is also not sufficient. Notwithstanding the impossibility of determining the value of λ, it appears very clearly that the two predictions, $h^2 \sim \epsilon$ and $t_\sigma \sim \epsilon^{-1/2a}$, are rather robust and indicate with very little uncertainty the location of the ideal glass transition.

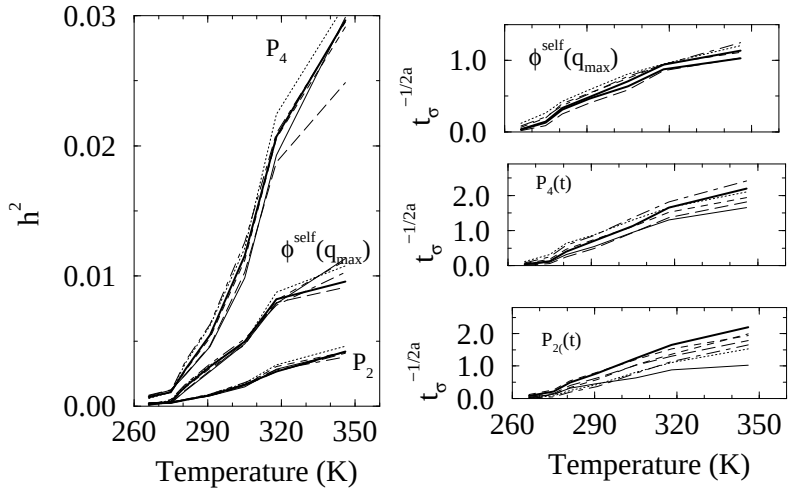


**Figure 6.** The $\epsilon$-dependences of the fitting parameters $h^2$ (left) and $t_\sigma^{-1/2a}$ (right) for some of the cases studied. The lines are labelled as in figure 5. The value of $a$ has been chosen consistently with the value of λ.

## 5. Conclusions

In this article we have critically examined the possibility of detecting unambiguously $\beta$-correlator behaviour in the time dependence of correlation functions close to the ideal glass transition. The important conclusion is that an unambiguous $\beta$-correlator behaviour cannot be observed if the distance from the ideal glass transition line is larger than $10^{-2}$. Since the role of the hopping processes increases on approaching the ideal glass transition point, a clear indication of the $\beta$-correlator can only by expected in systems, such as hard spheres, in which hopping is not a relevant transport mechanism. For realistic choices of the relative distance from the ideal glass transition point, a full description of the $\beta$-region requires also next-to-leading-order corrections to the asymptotic $\beta$-correlator of equation (1).

This should not be taken by any means as proving the MCT approach to the description of supercooled liquids to be invalid, because it has been by construction derived by means of an analysis of a fully solved MCT model, the hard-sphere case reported in references [3, 10]. Indeed, it is remarkable that the predicted dependence of the critical amplitude and the characteristic time of the $\beta$-correlator are so robust as to be correct even with imprecise choices of the value of $\lambda$. In all cases, an unambiguous estimate of the ideal glass transition point can be obtained.

The analysis presented in this article suggests that a MCT analysis of the liquid dynamics, restricted to the $\beta$-correlator (equation (1)), may lead to large errors in the determination of $\lambda$ [15]. The error can be significantly reduced if information on the $\alpha$-scaling is taken into account, since the exponent controlling the divergence of the $\alpha$-relaxation time on approaching the ideal glass transition line uniquely fixes the value of $\lambda$ [1, 2]. Indeed, previous work [7, 8] has shown that it is possible to describe self- and collective correlation functions (in both the $\beta$- and $\alpha$-regions) when next-to-leading-order corrections are taken into account and when the value of $\lambda$ is consistent with the $\alpha$-relaxation scaling. Thus, analysis of experimental and numerical data should always include information from the $\alpha$-relaxation scaling. The present findings strongly support the suggestion that the comparison between theory and experiment should be performed on a more extended level, i.e. by also evaluating the next-to-leading-order corrections or, even better, by comparing the full solution of the MCT equation with experimental or numerical work. Very relevant examples of such extended comparisons for simple liquids [16] have confirmed that MCT is able to describe in full detail the time and temperature dependence of correlations in the supercooled regime above the ideal glass transition line.

## Acknowledgments

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## References

[1] Götze W 1991 *Liquids, Freezing and Glass Transition (Les Houches Session LI, 1989)* ed J-P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland)
[2] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241
[3] Franosch T, Fuchs M, Götze W, Mayr M R and Singh A P 1997 *Phys. Rev.* E **55** 7153
[4] Cummins H Z, Du W M, Fuchs M, Götze W, Hildebrand S and Latz A 1993 *Phys. Rev.* E **47** 4223
[5] Du W M, Li G, Cummins H Z, Fuchs M, Toulouse J and Knauss L A 1994 *Phys. Rev.* E **49** 2192

[6] Baschnagel and Fuchs M 1995 *J. Phys.: Condens. Matter* **7** 6761
[7] Kob W and Andersen H C 1995 *Phys. Rev.* E **51** 4626
Kob W and Andersen H C 1995 *Phys. Rev.* E **52** 4134
Nauroth M and Kob W 1997 *Phys. Rev.* E **55** 675
[8] Sciortino F, Gallo P, Tartaglia P and Chen S-H 1996 *Phys. Rev.* E **54** 6331
Sciortino F, Fabbian L, Chen S H and Tartaglia P 1997 *Phys. Rev.* E **56** 5397
Fabbian L, Sciortino F, Thiery F and Tartaglia P 1998 *Phys. Rev.* E **57** 1485
[9] Lewis L J and Wahnström G 1994 *Phys. Rev.* E **50** 3865
[10] Fuchs M, Götze W and Mayr M R 1998 *Phys. Rev.* E **58** 3384
[11] Enhanced oscillations in the ps region have been observed in several molecular dynamics studies of supercooled liquids, especially close to the ideal glass transitions. Finite-size-effect studies have shown that these oscillations are spurious. For network-forming liquids there is evidence that the finite-size effects may be superimposed on a much weaker oscillation associated with the time domain manifestation of the boson peak.
[12] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241 and references therein
[13] Cummins H Z, Li G, Du W M and Hernandez J 1994 *Physica* A **204** 169 and references therein
[14] Tölle A, Wuttke J, Schober H, Randl O G and Fujara F 1998 *Eur. Phys. J.* B **5** 231 and references therein
[15] Fittings of experimentally measured correlation functions to different $\lambda$-values are reported by
Wuttke J 1993 *Z. Phys.* B **91** 357
[16] Gleim T, Kob W and Binder K 1998 *Phys. Rev. Lett.* **81** 4404
Nauroth M 1998 *PhD Thesis* University of Munich