

## Dynamics of colloidal glass-forming mixtures

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Recent experimental results from dynamic light scattering on two-component colloidal mixtures close to the glass transition are compared to theory. In the framework of the mode-coupling theory of the glass transition, close agreement is found in general. Discrepancies are identified for the minority-particle correlation function, and possible reasons for them are discussed.

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The quantitative description of dynamics in glass-forming liquids is a challenging task in condensed matter physics. To understand the underlying microscopic processes, one needs to consider systems as simple as possible. The hard-sphere system has been studied through colloidal suspensions [1–3], but there the glass transition is reached only due to the polydispersity in particle sizes [4]. Thus, binary mixtures are among the simplest model systems one can use in the study of nonquenched glass-transition dynamics. Computer simulations of Lennard-Jones and more complex mixtures [5] and experiments on colloidal mixtures [6] have been performed. Yet the effects that occur on mixing, i.e., how the glassy dynamics changes with changes in the mixture's composition, have not been studied systematically. Recently, Williams and van Meegen used a colloidal binary hard-sphere mixture (HSM) to study glassy dynamics [7]. Employing a two-color dynamic light scattering (DLS) technique [8,9], they could extract the time-dependent matrices of partial density correlation functions (PDCFs), providing data on a level of detail previously available only from computer simulations. Moreover, they gave a first systematic exploration of mixing effects on the glass-transition dynamics, thus presenting a challenging model system for testing theories of the glass transition.

This contribution deals with the question of how the mode-coupling theory of the glass transition (MCT) [10,11] performs as a *first principles* theory of the glass-transition dynamics in a HSM. A qualitative explanation of the observed anomalous mixing effects [7] has been published recently [12], but a quantitative comparison using the full theory was still missing, and in a similar study of a Lennard-Jones mixture [13], no mixture-composition dependence was discussed.

MCT for mixtures [14] has already been used to discuss a number of systems [12,15–19]. Computer simulation results for a Lennard-Jones mixture [13,20] and models of a silica melt [21] and a metallic melt [22] have been analyzed quantitatively with success. MCT yields an equation for the matrix of PDCFs,  $\Phi_{\alpha\beta}(q,t) = \langle \delta\varrho_{\alpha}^*(\vec{q},t) \delta\varrho_{\beta}(\vec{q},0) \rangle$ , where  $\langle \cdot \rangle$  is the canonical average and  $\delta\varrho_{\alpha}(\vec{q},t) = \sum_k \exp[i\vec{q} \cdot \vec{r}_k^{(\alpha)} \times(t)] / \sqrt{N}$  are the number density fluctuations at wave vector  $\vec{q}$  in species  $\alpha$  in a system with  $N = \sum_{\alpha} N_{\alpha}$  particles. Isotropy implies that  $\Phi_{\alpha\beta}(q,t)$  depends on  $\vec{q}$  through  $q = |\vec{q}|$  only. The time evolution of the system will be governed by Smoluchowski dynamics, as usual for colloidal systems [23]. Denoting matrices by bold symbols, the equation of motion reads [14]

$$\tau_q \dot{\Phi}_q(t) + \mathbf{S}_q^{-1} \Phi_q(t) + \int_0^t \mathbf{M}_q(t-t') \dot{\Phi}_q(t') dt' = \mathbf{0}. \quad (1)$$

The  $\tau_{\alpha\beta,q} = 1/(q^2 D_{\alpha}^0) \delta_{\alpha\beta}$  are given by the short-time diffusion coefficients  $D_{\alpha}^0$ , and  $\mathbf{S}_q$  is the matrix of partial static structure factors,  $\mathbf{S}_q = \Phi_q(t=0)$ . Equation (1) is closed in MCT by

$$M_{\alpha\beta}(q,t) = \int \frac{d^3k}{(2\pi)^3} \sum V_{\alpha\beta}^{\alpha'\beta'\alpha''\beta''}(\vec{q},\vec{k},\vec{p}) \times \Phi_{\alpha'\beta'}(k,t) \Phi_{\alpha''\beta''}(p,t), \quad (2)$$

where the sum runs over all repeated indices, and  $\vec{p} = \vec{q} - \vec{k}$ . The vertices  $V$  can be worked out in detail [12]; they are determined by the equilibrium structure, and after some technical approximation are given by  $\mathbf{S}_q$  alone. For this latter quantity, the Percus-Yevick approximation [24] will be used, which gives the simplest theory without free parameters suitable for hard-sphere mixtures at high densities. Equations (1) and (2) are solved numerically on a grid of  $M = 200$  equidistantly distributed wave vectors  $q = 0.2, \dots, 79.8$  as described previously [12]. I have checked that the numerical parameters chosen do not affect qualitative features of the results. The diameters of the spheres will be denoted  $d_{\alpha}$ , and  $\varrho$  is the total number density. The binary HSM will be characterized by the total packing fraction  $\varphi = \varphi_A + \varphi_B$ ,  $\varphi_{\alpha} = (\pi/6)(N_{\alpha}/N)\varrho d_{\alpha}^3$ ; the diameter ratio of small ( $B$ ) to large ( $A$ ) spheres,  $\delta = d_B/d_A$ ; and the packing contribution of small spheres,  $\hat{x}_B = \varphi_B/\varphi$ . The short-time dynamics, given by  $\tau_q$  in Eq. (1), is assumed to follow the Stokes-Einstein relation  $D_{\alpha}^0 \sim 1/d_{\alpha}$ .

Time-dependent quantities will be discussed as functions of reduced time  $t/\hat{\tau}$ , where  $\hat{\tau} = d_A^2/(24D_A^s)$  is a characteristic “Brownian” time involving the measured short-time diffusion constant of the large particles,  $D_A^s$ . The latter is, in colloidal suspensions, different from  $D_A^0$  due to solvent-mediated hydrodynamic interactions (HIs) [23]. To test the assumption of MCT that HIs merely influence the overall time scale [25], let us incorporate them by rescaling  $D_{\alpha}^0$  in Eq. (1); for the data discussed below, I find satisfactory results by setting  $D_A^s/D_A^0 \approx 0.2$ . Still the MCT description of the dynamics at short times,  $t/\hat{\tau} \leq 1$ , say, cannot be expected to be accurate, since the approximation is tailored for long times.

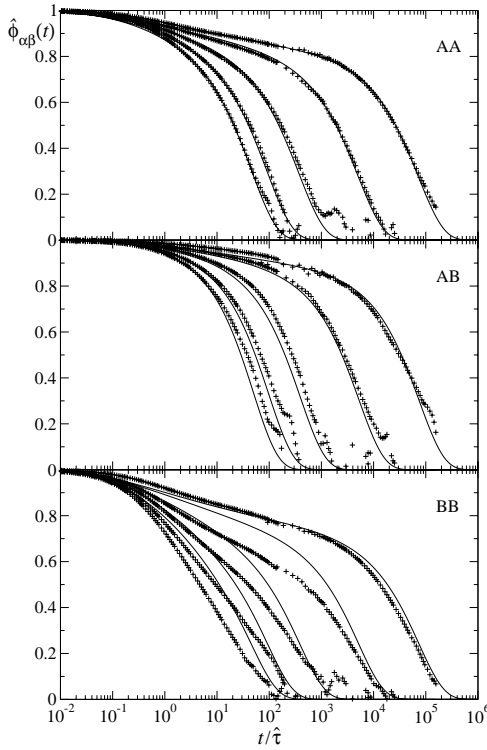


FIG. 1. Normalized partial density correlation functions  $\hat{\phi}_{\alpha\beta}(q,t) = \Phi_{\alpha\beta}(q,t)/S_{\alpha\beta}(q)$  for a binary hard-sphere mixture with size ratio  $\delta=0.6$  and packing contribution of the smaller species  $\hat{x}_B=20\%$ . Crosses are experimental results for  $qd_A=6.0$  and total packing fractions  $\varphi_{\text{expt}}=0.58, 0.57, 0.55, 0.53,$  and  $0.51$  (from right to left, from Ref. [7]). Solid lines are MCT results for  $qd_A=5.4$  and  $\varphi_{\text{MCT}}=0.516, 0.510, 0.497, 0.475,$  and  $0.460$ .

MCT results for the PDCFs at  $\delta=0.6$ ,  $\hat{x}_B=0.2$ , and several packing fractions  $\varphi$  are shown in Fig. 1 as solid lines. The crosses denote the experimental data corresponding to the same  $(\delta, \hat{x}_B)$  from Ref. [7]. These data refer to a scattering wave vector  $qd_A=6.0$ , while the MCT results are shown for  $qd_A=5.4$ . This shift in wave vector accounts for a 10% error in the predicted wave-vector dependence of the frozen glassy structure [2].

Since the MCT result for the glass-transition packing fraction of a hard-sphere system is in error by about 10% [26], one has to correct for this by comparing theory to experiment not at the same  $\varphi$ , but at the same separation from the glass-transition singularity. Technically,  $\varphi_{\text{MCT}}$  entering the MCT equations has been treated as a fit parameter. The resulting relation between  $\varphi_{\text{MCT}}$  and  $\varphi_{\text{expt}}$  is plotted in Fig. 2; it can be approximated by a  $\hat{x}_B$ -independent shift  $\varphi_{\text{expt}} \approx \varphi_{\text{MCT}} + 0.05 \pm 0.005$ . There is, however, a slight systematic deviation: the  $\varphi_{\text{MCT}}$  are lower for higher  $\hat{x}_B$ , implying that the time scale for the final relaxation process decreases with increasing  $\hat{x}_B$ . But this is precisely what MCT predicts for the present mixture even at constant  $\varphi_{\text{MCT}}$  [12]. Thus the theory explains, but underestimates, this so-called plasticization effect.

There is satisfactory agreement between theory and experiment for the colloidal binary HSM at  $\delta=0.6$  and  $\hat{x}_B=0.2$  in the autocorrelator of the majority species,  $\hat{\phi}_{AA}$ , and

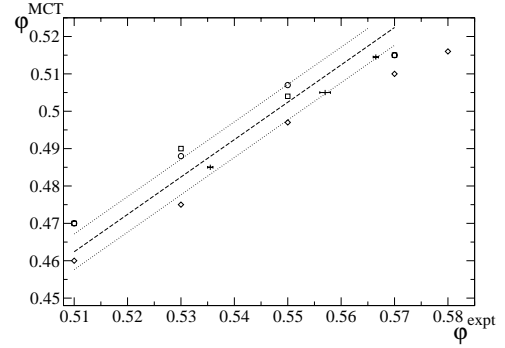


FIG. 2. Packing fractions  $\varphi_{\text{MCT}}$  versus experimental ones  $\varphi_{\text{expt}}$  used in the fits to the data of Refs. [7] and [6]; concentrations of small spheres are  $\hat{x}_B=20\%$  (diamonds),  $10\%$  (squares), and  $5\%$  (circles) for the  $\delta=0.6$  mixtures, and  $12\%$  (cross symbols) for the  $\delta=0.8$  mixture. The dashed line represents a shift,  $\varphi_{\text{expt}} \approx \varphi_{\text{MCT}} + 0.05$ ; dotted lines indicate 1% variation in  $\varphi_{\text{MCT}}$ .

the cross-correlator  $\hat{\phi}_{AB}$ . The PDCFs are reproduced over the whole experimentally accessible time window for times  $t/\tau \gtrsim 1$ . The *BB* correlator in the lower panel of Fig. 1, however, shows pronounced disagreement; the data are systematically smaller than the calculated curves at all times. Let us investigate this point in more detail, tracing it back to a MCT-independent question.

Highly charged colloids set aside, one expects the Smoluchowski operator to describe the dynamics in colloidal suspensions for times long compared to the Brownian time scale [23,27]. In a one-component system this induces the density correlation functions to be superpositions of decaying exponentials with positive weights only. In multicomponent PDCFs as a whole, with the term “positive” replaced by “positive definite.” One can show that the MCT approximation exactly preserves this direct consequence of the mathematical structure of the Smoluchowski operator [28]. This guarantees that all MCT solutions shown here represent the three independent elements of a  $2 \times 2$  matrix that is positive definite for all times  $t$  and for each given  $\varphi$ . To test whether this is true for the experimental data, one needs to undo the normalization  $\hat{\phi}_{\alpha\beta}(q,t=0)=1$ , which in turn requires knowledge of the partial static structure factors  $S_{\alpha\beta}(q)$ . These are difficult to obtain from DLS, so let us take instead the Percus-Yevick results used for the MCT calculation; the following argument is insensitive to the precise values chosen. One way to check the positive definiteness of the  $2 \times 2$  matrices is to test the condition  $e_{\pm}(q,t) \geq 0$  for the two eigenvalues for all  $t$ . We plot these quantities in Fig. 3 for the experimental data shown in Fig. 1. One finds for  $\varphi_{\text{expt}} \leq 0.57$  a slightly negative smaller eigenvalue for times exceeding  $t/\tau \approx 10$ , in violation of the positive definiteness of  $\Phi_{\text{expt}}(q,t)$ . Thus the data contradict the assumption that the PDCFs are purely relaxing functions in this time window, i.e., they are in disagreement with the assumption of Smoluchowski dynamics. For this reason, they cannot be described by MCT or any theory that describes the long-time glassy dynamics as structural relaxation. Only for  $\hat{x}_B=0.2$  and  $\varphi_{\text{expt}}=0.58$  do the eigenvalues both stay positive in the structural relaxation regime; con-

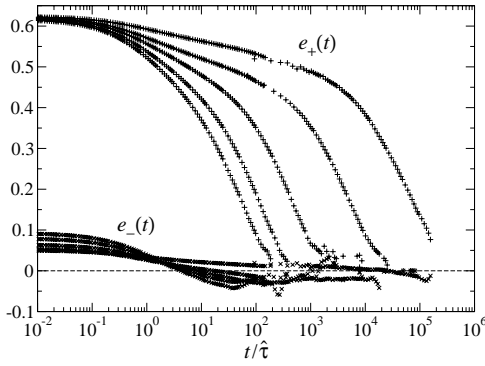


FIG. 3. Eigenvalues  $e_+(q,t)$  (upper) and  $e_-(q,t)$  (lower curves) of the experimentally measured matrices of partial correlation functions  $\Phi(q,t)$  shown in Fig. 1. See text for details.

comitantly, this is the only data set I have been able to fit completely. In the other cases the violation of positive definiteness is only of the order of 5%; it is about as large as the deviation seen in the lower panel of Fig. 1 and probably inside the error bars for the *BB* correlator measurements [29]. Indeed, the fits shown in Fig. 1 demonstrate that the violation of positive definiteness arises mostly from the *BB* correlations, since both the *AA* and *AB* correlators can be fitted with a theory that yields positive definite PDCFs at all times. Note that the *BB* correlators contribute much less, by a factor of about 2–5, than the *AA* and *AB* to the scattering signal from which the experimental PDCFs are extracted [29].

For the  $\delta=0.60$ ,  $\hat{x}_B=20\%$  mixture, data have also been reported in Ref. [7] for different scattering wave vectors  $q$ . Figure 4 shows the experimental results for the large-large (*AA*) correlation functions at  $\varphi_{\text{expt}}=0.58$  as in Fig. 1, but also for  $qd_A=3.0$  and  $7.2$ . They are analyzed in the same spirit as above, adjusting the wave vectors slightly to  $qd_A=3.8$  and  $7.0$  in the MCT calculation. As is apparent from Fig. 4, MCT captures the detailed statements about the local structure of the glass-forming mixture inherent in the  $q$ -dependent correlation functions. Only for the smallest  $q$  shown is the agreement slightly worse, and the adjustment of the  $q$  value exceeds the 10% level.

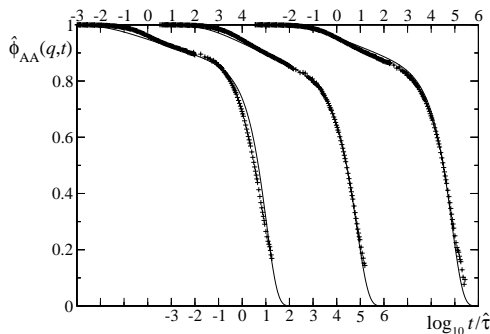


FIG. 4. Crosses denote experimental data as in the upper panel of Fig. 1, but for  $qd_A=3.0$  (left),  $6.0$  (middle), and  $7.2$  (right). Solid lines are MCT results for  $qd_A=3.8$ ,  $5.4$ , and  $7.0$ , respectively. For clarity, the different sets of curves have been translated along the  $t$  axis as indicated by the labels.

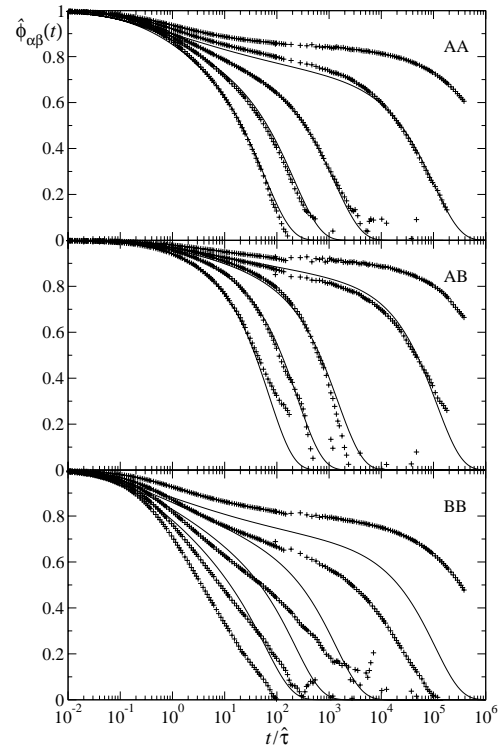


FIG. 5. Experimental data and MCT calculations for a binary hard-sphere mixture with  $\delta=0.6$  and  $\hat{x}_B=10\%$ , otherwise as in Fig. 1. Values for  $\varphi_{\text{expt}}$  ( $\varphi_{\text{MCT}}$ ) are  $0.58$ ,  $0.57$  ( $0.515$ ),  $0.55$  ( $0.504$ ),  $0.53$  ( $0.490$ ), and  $0.51$  ( $0.470$ ), from right to left.

So far, only data for a single mixture composition have been analyzed here. Let us demonstrate the effect of a composition change, by considering in Fig. 5 results for  $\hat{x}_B=0.1$ ; they are similar to those for  $\hat{x}_B=0.05$ . Again, the data for the *AA* and *AB* correlators compare favorably to the calculated curves, at least for  $\varphi_{\text{expt}} \leq 0.57$ . The *BB* correlator data are not reproduced by the theory, and a more detailed analysis of the required positive definiteness reveals a similar picture as discussed in connection with Fig. 3. For the highest packing fraction  $\varphi_{\text{expt}}=0.58$ , it has not been possible to reproduce the experimental data convincingly at all. Problems arise stemming from an increasing discrepancy in the height of the plateaus in the PDCFs at intermediate times. The same situation arises also for  $\hat{x}_B=0.05$ . Currently, one can only speculate about the origin of this deterioration of fit quality with decreasing  $\hat{x}_B$ . Note that the intrinsic size polydispersity of both particle species is not accounted for in the theory.

It is also instructive to investigate changes in the third control parameter of the binary hard-sphere mixture, viz., the size ratio  $\delta$ . From light-scattering experiments, the PDCFs have been obtained only for the  $\delta=0.6$  case, but Henderson *et al.* [6] have studied two polydisperse colloidal hard-sphere suspensions that can be approximated by a monodisperse system and by a binary mixture with  $\delta=0.8$  and  $\hat{x}_B \approx 0.12$ , respectively. In this study, results for the scattering function

$$\phi^m(q,t) \propto \sum_{\alpha\beta} b_\alpha(q) \Phi_{\alpha\beta}(q,t) b_\beta(q) \quad (3)$$



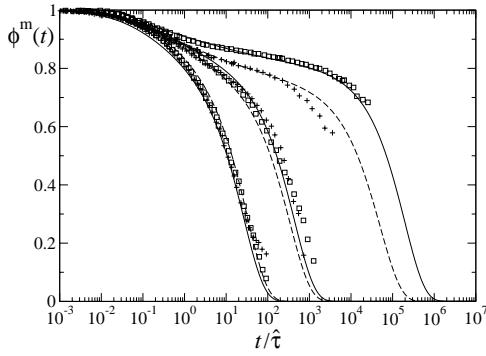


FIG. 6. Plus symbols are the experimental data from Ref. [6] for the scattering function  $\phi^m(q,t)$  [cf. Eq. (3)] in a nearly monodisperse colloidal hard-sphere system, at packing fractions  $\varphi=0.535$ , 0.558, and 0.567, from left to right. Squares are data for a bidisperse system with size ratio  $\delta=0.8$  and  $\hat{x}_B \approx 0.12$ , at  $\varphi=0.536$ , 0.556, and 0.566. The dashed (solid) lines are MCT calculations for a monodisperse (binary) hard-sphere system with  $\varphi=0.485$ , 0.505, and 0.5145, for wave vector  $qd_A=6.6$  (7.4).

have been reported, where  $b_\alpha(q)$  are the scattering amplitudes, or single-particle form factors, for wave vector  $q$  and species  $\alpha$ . In principle, knowledge of these  $b_\alpha(q)$  would enable us to calculate the theoretical result for  $\phi^m(q,t)$  from the PDCF  $\Phi_{\alpha\beta}(q,t)$ . For simplicity, let us assume that the colloidal particles are ideal uniform spheres of homogeneous refractive index. Then the scattering amplitudes are given as [23]

$$b_\alpha(q) \propto \frac{d_\alpha^3}{(qd_\alpha)^3} \left( \sin(qd_\alpha/2) - \frac{qd_\alpha}{2} \cos(qd_\alpha/2) \right). \quad (4)$$

Figure 6 compares some results from Ref. [6] with the corresponding MCT results obtained from Eqs. (1)–(4), normalized to  $\phi^m(q,t=0)=1$ . The curves refer to a wave vector close to the first peak of the (total) static structure factor, i.e.,  $qd_A=6.6$  and 7.4 for the MCT results for the one-component and the binary system, respectively. As above, the short-time diffusion coefficient in the theory has been adjusted, in this case to  $D_A^s/D_A^0 \approx 0.27$ . In Fig. 6, the plus symbols (squares) are experimental results for the monodisperse (binary) system, taken at three packing fractions that are as close as possible for the two systems. The dashed (solid) lines are the corresponding MCT results, while here the packing fractions have been chosen exactly equal. Again the agreement is quite satisfactory in both cases. Note that the description of the monodisperse system at the highest packing fraction shown could be improved, if one allows the values of  $\varphi$  to differ slightly in the MCT calculations, as they

do for the experimental data. As in the  $\delta=0.6$  case, an overall shift in the packing-fraction values has been allowed for. The resulting values are plotted in Fig. 2, where they can be seen to agree well with the ones used in the  $\delta=0.6$  fits.

Note that the fits presented in Fig. 6 exhibit a qualitatively different trend from that observed for the  $\delta=0.6$  mixtures of Ref. [7]: while in the latter case increasing the contribution of smaller particles at fixed total packing fraction led to a marked decrease in the final relaxation times, the  $\delta=0.8$  case of Fig. 6 shows a slowing down of the relaxation upon increasing the contribution of smaller particles from  $\hat{x}_B=0$  to  $\hat{x}_B \approx 0.12$ . This is consistent with a recent MCT prediction [12] that there exist two different scenarios for the dependence of the glass-transition packing fraction on mixture composition; one for moderate size disparity, where mixing stabilizes the glass, and one for more pronounced size disparities, where mixing stabilizes the liquid.

In conclusion, I have applied the mode-coupling theory of the glass transition to a binary hard-sphere mixture and compared to it the partial density correlation functions obtained recently by dynamic light scattering on colloidal hard-sphere mixtures with size ratio  $\delta=0.6$  [7]. Close overall agreement is found, if one allows for about 10% deviation in three overall quantities, viz., the packing fraction  $\varphi$ , the wave-vector magnitude  $q$ , and the short-time diffusion constant  $D_A^s$ . In general, the analysis presented here underlines the applicability of MCT to describe mixture-specific effects found in typical glass-forming colloidal suspensions. The same is found for light-scattering data on a mixture with size ratio  $\delta=0.8$  [6], and altogether the results hint at the presence of two different mixing scenarios, depending on the size ratio, as predicted by the theory.

The small-particle correlation function  $\hat{\phi}_{BB}(q,t)$  shows disagreement between experiment and theory: the experimentally obtained  $BB$  correlators show faster decay than predicted by the theory. This is, however, not necessarily a failure of MCT. Since the present data are not in accord with the positive definiteness of the relaxation functions expected for structural relaxation in general, they also do not fit into the concepts of a potential energy landscape that are commonly used to discuss glassy dynamics [30,31]. The deviations might be due to a magnification of small errors, as was explained in connection with Fig. 3. Thus it appears that further experimental or computer simulation investigations of this issue are desirable.

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