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High-temperature dynamics in glass-forming liquids

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The light scattering spectra of several recently investigated glass-forming systems are reanalyzed. The analysis shows that for both fragile and nonfragile glass-forming liquids, there is some general scenario for the dynamics at high temperatures that seems to follow the qualitative scenario suggested by the mode-coupling theory (MCT) of the liquid-glass transition. However, significant quantitative deviations from MCT predictions occur. They are small for fragile and large for nonfragile systems. Moreover, from the analysis a dynamic crossover temperature clearly appears as a universal feature and in all cases it is close to the critical temperature reported within standard MCT analyses.

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I. INTRODUCTION

During the last decade investigations of the glass-transition phenomenon were strongly stimulated by the achievements of the mode-coupling theory (MCT) [1]. The latter was developed for simple liquids and predicts a dynamic transition from liquidlike to solidlike (amorphous) behavior at some critical temperature T_c. Several authors have compared neutron and light scattering data of fragile liquids with MCT predictions and obtained good agreement. The dynamic crossover temperature T_c has been identified to be 15–25% higher than the conventional glass-transition temperature T_g [2–7].

In spite of these encouraging results recently some authors questioned the standard way to identify the dynamic crossover temperature, in some cases even the presence of a crossover is doubted [8,9]. The crossover temperature cannot be directly found in the experimental data presented so far: the spectra change smoothly around T_c and only an analysis in the framework of the theory provides access to determining this critical temperature T_c. The latter makes the MCT predictions weak. Another criticism [8] is related to the quantitative disagreements of MCT predictions for the susceptibility spectrum, which have been found in the light scattering spectra of $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (CKN), and salol [4,5]. Furthermore, strong deviations from MCT predictions have been found for the nonfragile liquid glycerol, but the origin of those discrepancies is still an open question [7,10].

In the present communication we suggest an analysis of the dynamics which is inspired by the qualitative scenario predicted by MCT. Within this concept we will reanalyze published data for both fragile and nonfragile systems at temperatures above and below T_c. Our analysis shows that deviations from the quantitative predictions of MCT appear already in fragile systems. The deviations increase with decreasing degree of fragility. A general scenario involving power law dependencies of the susceptibility spectra is found for fragile and nonfragile systems at high temperatures resembling the qualitative picture suggested by MCT. Moreover, a crossover temperature can be clearly identified from the experimental data using our analysis.

II. MCT PREDICTIONS

Let us recall here the main predictions of MCT in its idealized version for the high temperature dynamics of a supercooled liquid ($T > T_c$) [1]. MCT considers the density-density correlation function $F_q(t)$. A two-step relaxation is predicted for $F_q(t)$, including a fast process with a characteristic time scale in the picosecond region and a slow process (α process), of which only the latter is strongly temperature dependent. In the frequency domain MCT analyzes the dynamic susceptibility $\chi''(\omega)$. The existence of separate slow and fast processes leads to a minimum in $\chi''(\omega)$. Power law dependencies are predicted for both processes: $\chi''(\omega) \propto \omega^a$ for the low-frequency tail of the fast dynamics and $\chi''(\omega) \propto \omega^{-b}$ for the high frequency tail of the α relaxation [1]. MCT predicts that at $T > T_c$ the spectral shapes and intensities of both processes are essentially temperature independent. The only temperature variation is the one of the α-relaxation time τ_α. This scenario is qualitatively sketched in Fig. 1.

The first consequence of this simple picture is that the minimum between α process and fast dynamics at different temperatures has a universal form which can be approximated by a sum of two power laws

$$\chi''(\omega) = \chi''_{\min} \frac{\{b(\omega/\omega_{\min})^a + a(\omega/\omega_{\min})^{-b}\}}{(a+b)} . \tag{1}$$

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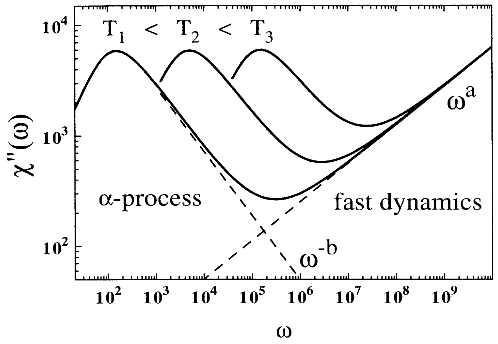

FIG. 1. Schematic representation of the temperature evolution predicted by MCT for the susceptibility spectra at $T > T_c$ [1].

This means, that the data around the minima can be reduced to a master curve. Furthermore, the temperature variations of the parameters characterizing the minimum, the amplitude $\chi''_{\min}$ and the position $\omega_{\min}$ are interrelated

$$\chi''_{\min} \propto (\omega_{\min})^a . \tag{2}$$

The variation of these parameters are also related to the time of the α-relaxation $\tau_\alpha = (\omega_\alpha)^{-1}$

$$\omega_{\min} \propto (\omega_\alpha)^\kappa \text{ and } \chi''_{\min} \propto (\omega_\alpha)^\mu , \tag{3}$$

where $\kappa = b/(a+b)$ and $\mu = ab/(a+b)$. (Here we want to note that in discussing similar relations an error appeared in Eq. (15) of Ref. [7].)

We would like to stress at this point that Eqs. (1)–(3) follow from the predictions: (i) intensity and spectral shape of the fast dynamics and also of the α process are fixed and only τ_α varies significantly with T; (ii) power laws describe the tails of the two processes.

In addition MCT makes the important and nontrivial prediction that the exponents a and b fulfill the relation

$$\lambda = \frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)} , \tag{4}$$

where $\Gamma(x)$ is the gamma function. Thus the so-called exponent parameter λ fixes all exponents. In addition the value of the exponents has to be $0 < a < 0.395$ and $0 < b < 1$. One should keep in mind that these formulae are asymptotic expressions of the full MCT equations [1]. The idealized version of MCT predicts also that the time of the α process exhibits a critical temperature dependence

$$\tau_\alpha \propto (T - T_c)^{-\gamma} \text{ with } \gamma = \frac{1}{2a} + \frac{1}{2b} . \tag{5}$$

Then the well known prediction of a critical temperature dependence for the minimum parameters follows from Eqs. (3) and (5):

$$(\omega_{\min})^{2a} \propto (T - T_c) \text{ and } (\chi''_{\min})^2 \propto (T - T_c) . \tag{6}$$

These MCT predictions are in reasonable agreement with light and neutron scattering spectra of calcium potassium nitrate (CKN) [2,4], O-terphenyl (OTP) [3,6], and salol [5]. However, in the nonfragile system glycerol, MCT fails to describe the spectra [7,10].

Of course, the time of the α process does not diverge in real systems nor does it follow the relation given in Eq. (5) [11]. In order to overcome the first discrepancy, the theory has been extended to include also the so-called hopping diffusion which restores ergodicity below T_c. However, even in the extended theory the predictions of the idealized version [Eqs. (1)–(4)] are expected to be sufficient for describing the experimental data well above T_c [13].

Below T_c, MCT predicts that the spectral shape of the fast dynamics changes, in particular, its integrated intensity starts to decrease. The latter prediction is the so-called anomaly of the Debye-Waller factor which has been exploited by the early neutron scattering experiments in order to identify T_c [2,3]. Thus, Eqs. (1)–(3) are expected to fail, and consequently, T_c can be identified as the point at which first deviations from the predictions occur while cooling the liquid.

III. REANALYSIS OF EXPERIMENTAL DATA

The traditional way of analyzing data in the framework of MCT is to collapse the data around the minimum of $\chi''(\omega)$ into a master curve and then interpolate it by a sum of two power laws [Eq. (1)] while keeping the relation between exponents a and b fixed by Eq. (4). We call these exponents a_{MCT} and b_{MCT}, respectively. Then the temperature dependence $\chi''_{\min}$ and $\omega_{\min}$, and τ_α are checked for consistency. Such master curves are shown in Fig. 2 for OTP [6], m-tricresyl phosphate (m-TCP) [7], and glycerol [7]. The degree of fragility m [12]

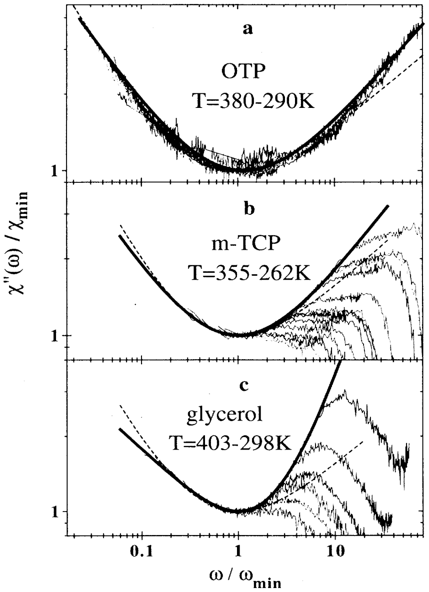

FIG. 2. The master curves for $\chi''(\omega)$ in OTP (a), m-TCP (b) and glycerol (c). Thin solid lines: experimental spectra; dashed line: MCT interpolation with a_{MCT} and b_{MCT}; thick solid line: interpolation with free exponents a_{free} and b_{free}. The values of the exponents are listed in Table I.

TABLE I. Extracted exponents for several glass-forming liquids.

		Master curve analysis [Eq. (1)]				Crosstest [Eq. (2)]		
		MCT fit		free fit				
Liquid	m	a_{MCT}	b_{MCT}	a_{free}	b_{free}	a_{eff}	$a_{\mathrm{eff}}/a_{\mathrm{MCT}}$	Ref.
1. CKN	94	0.273	0.458	—	—	0.34	1.25	[4]
2. OTP	81	0.33	0.65	0.45	0.55	0.44	1.33	[6]
3. *m*-TCP	76	0.35	0.72	0.50	0.57	0.47	1.34	[7]
4. Salol	63	0.33	0.64	—	—	0.46	1.39	[5]
5. Glycerol	58	0.34	0.71	1.1	0.37	1.12	3.3	[7]
		0.32	0.61	—	—			[10]

changes within this series. In all cases deviation from the envelope predicted by MCT is observed at the high frequency side of the minimum. The deviations are weak for OTP, larger for *m*-TCP and very strong for glycerol. On the other hand, a much better interpolation of the master curve can be achieved if free [i.e., not restricted by Eq. (4)] exponents a and b are chosen as is demonstrated in Fig. 2. The value a_{free} is always larger than a_{MCT} (cf. Table I) and out of the range of validity of a_{MCT} in MCT.

As pointed out, one can also check the basic MCT prediction by analyzing the relation between χ''_{min} and ω_{min} [Eq. (2)]. This has been done already for CKN [4], salol [5], and OTP [6]. In all cases deviations from the value of the exponent a_{MCT} predicted by MCT were found. We summarize these data in Fig. 3, however, we do not restrict the analysis to high temperatures as it is usually done but we also include data for temperatures below the reported T_c. Clearly, the data follow straight lines at high temperatures, only at the lowest temperatures (corresponding to the lowest χ''_{min} and ω_{min} values in Fig. 3) strong deviations occur. However, the slope of the lines give an effective exponent a_{eff} which is significantly higher than the value a_{MCT}. The deviation systematically increases with the decrease of the degree of fragility: it starts from $a_{\mathrm{eff}}/a_{\mathrm{MCT}}=1.25$ for the fragile CKN and raises up to $a_{\mathrm{eff}}/a_{\mathrm{MCT}}=3.3$ for the nonfragile system glycerol. On the other hand, a_{eff} is close to the value a_{free}, which has been found from the free fit of the master curves in Fig. 2 (cf. also Table I).

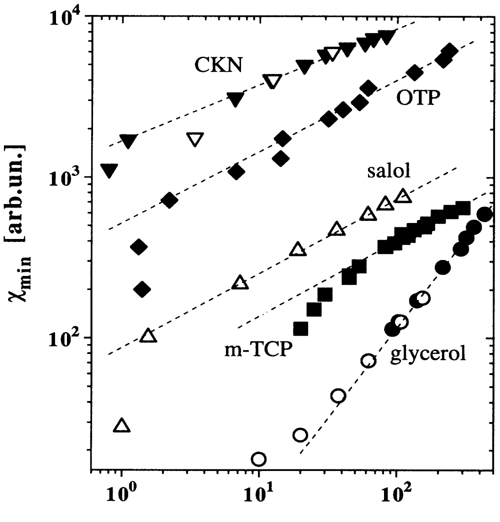

FIG. 3. χ''_{min} plotted versus ω_{min}: (▼) [4] and (▽) neutron data [2] for CKN; (◆) OTP [6], (△) salol [5], (■) *m*-TCP [7], (●) [7] and (○) [10] glycerol. Dashed lines show power law behavior with slope a_{eff} (the values are presented in Table I).

Another consequence of the qualitative MCT scenario can also be checked, namely, Eq. (3). Here ω_{min} or χ''_{min} is related to the frequency ω_α. Again this was previously analyzed for CKN [4], salol [5], and OTP [6] and small deviations from the MCT predictions were found. In the cases of the less fragile systems *m*-TCP and glycerol strong deviations are found, especially for ω_{min} versus ω_α as is demonstrated in Fig. 4. At high temperatures the

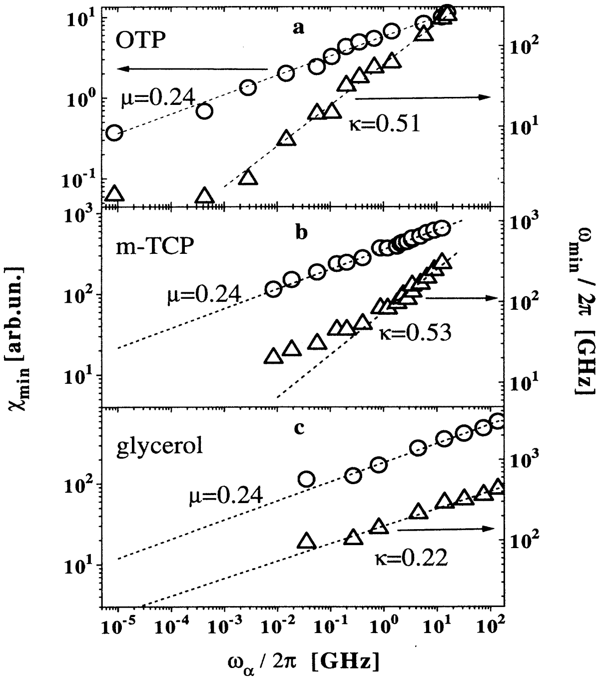

FIG. 4 χ''_{min} and ω_{min}, respectively, plotted versus ω_α: (a) OTP, $\mu_{\mathrm{MCT}}=0.22$ and $\kappa_{\mathrm{MCT}}=0.67$ (expected by MCT using the exponents a_{MCT} and b_{MCT}); $\mu_{\mathrm{free}}=0.25$ and $\kappa_{\mathrm{free}}=0.55$ (using a_{free} and b_{free}), (b) *m*-TCP, $\mu_{\mathrm{MCT}}=0.23$ and $\kappa_{\mathrm{MCT}}=0.68$; $\mu_{\mathrm{free}}=0.27$ and $\kappa_{\mathrm{free}}=0.53$, (c) glycerol $\mu_{\mathrm{MCT}}=0.23$ and $\kappa_{\mathrm{MCT}}=0.68$; $\mu_{\mathrm{free}}=0.28$ and $\kappa_{\mathrm{free}}=0.25$.

predicted power law is found in all cases, but the exponent κ deviates from the one forecasted by MCT (using a_{MCT} and b_{MCT}). However, reasonable agreement with the experiment appears if one applies a_{free} and b_{free} (cf. Table I, Fig. 4). Also in Fig. 4 it is seen that at the lowest temperatures, deviations from the power law behavior appear.

IV. DISCUSSION AND CONCLUSIONS

From the analysis presented above we summarize the following observations:

(i) For all glass forming liquids analyzed, the high temperature data around the susceptibility minimum can be collapsed onto a master curve which is reasonably well interpolated by a sum of two power laws. However, the extracted exponents a and b do not follow the relationship [Eq. (4)] predicted by MCT. In fragile systems the deviations are small, and they increase with decreasing degree of fragility.

(ii) The relation between χ''_{min} and ω_{min} follows a power law [Eq. (2)]. The corresponding exponent a is larger than predicted by MCT, and it is close to the one obtained from a free fit of the master curve. Furthermore, checking the relationships [Eqs. (3)] connecting the minimum parameters with the time of the α process, again consistency is only provided by introducing the exponents a_{free} and b_{free} instead of a_{MCT} and b_{MCT}.

(iii) At lower temperatures, strong deviations appear from the power law behavior found at high temperatures, in other words a qualitative change occurs.

From all these findings we conclude that the qualitative pictures sketched in Fig. 1 holds above a certain temperature: the fast dynamics are fixed in time and amplitude, the α process keeps its spectral shape and amplitude and only its characteristic time τ_α varies with temperature. The spectrum can be approximated by the sum of these two processes, and the exponents a and b are virtually temperature independent. This scenario holds for both fragile and nonfragile glass formers and it is just the same as the qualitative scenario suggested by MCT for temperatures above T_c. MCT also predicts a relation between the exponents a and b [Eq. (4)], however, this relation is not observed. In all cases the exponent a is found to be larger and in most cases out of the range of validity as it is expected from MCT. Therefore, we conclude that the spectrum of the fast dynamics does not follow the MCT predictions. The discrepancy is the higher the stronger the glass former is.

We would like to note that the authors of Ref. [13] suggested another explanation for this discrepancy. They ascribed it to an additional temperature dependence of the intensity of the fast relaxation. Using this assumption the authors explained the results for CKN and salol (later also for propylene carbonate [14]), where the deviations are weak. However, it can be hardly the case for glycerol, where the deviations are extremely strong (Figs. 2–4). Moreover, with this assumption one would expect the deviations for the crosstest χ_{min} vs ω_α to be stronger than for ω_{min} vs ω_α, but the experimental results (Fig. 4) shows just the reverse situation. These deviations are not related to the peculiarities of light scattering, because the same deviations for the exponent a have been found in neutron scattering experiments: for CKN a_{eff} is similar, or even higher than the light scattering data (Fig. 3), for OTP it was found that $a \approx 0.45$ gives better agreement for the estimation of T_c [3] and $a \approx 1$ has been found in neutron spectra of glycerol [10].

Another phenomenological description of the depolarized light scattering spectra of OTP was suggested in [15]. The authors identified an additional "fast process" with a characteristic frequency ~30 GHz which is not identical with what we call here "fast process" with a characteristic frequency 10^2–10^3 GHz. However, at high temperatures this contribution merges with the tail of the α relaxation and disturbs our analysis only weakly (Figs. 2–5): all high temperature ($T > 290$ K) data for OTP can be consistently described in the framework of the qualitative picture Fig. 1, Eqs. (1)–(3).

As mentioned, within MCT a significant change of the dynamics is expected to set in below T_c, e.g., the amplitude of the fast dynamics starts to decrease, whereas above T_c it is constant. Furthermore, the spectral shape of the fast dynamics changes. Accordingly the simple picture of Fig. 1 breaks at $T < T_c$. This change is a nontrivial prediction and the only quantity in which the dynamic transition is directly reflected. Thus it is tempting to conclude that this change in the dynamics is the reason for the deviations observed at the low temperatures in Figs. 3–4.

In order to identify the crossover temperature at which the high temperature scenario of Fig. 1 breaks, we plot $Y = [\ln(\chi''_{\mathrm{min}}) - a_{\mathrm{eff}} \ln(\omega_{\mathrm{min}})]$ versus temperature in Fig. 5. In all cases we find a crossover temperature which is vir-

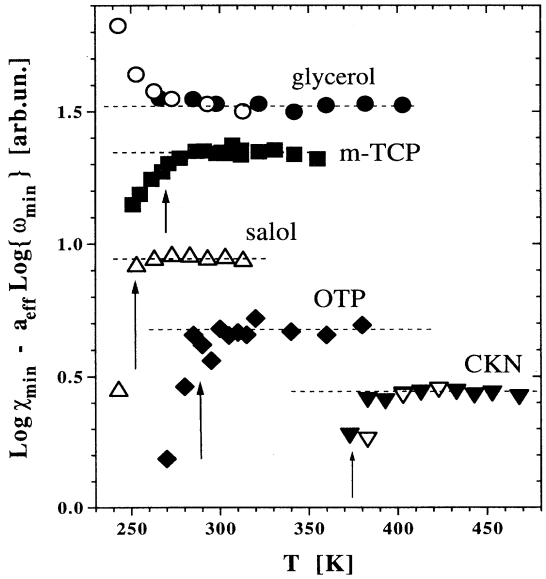

FIG. 5. Temperature dependence of the relation between the minimum parameters [Eq. (2)]. Symbols are the same as in the Fig. 3. The arrows indicate the critical temperature T_c as reported by standard MCT analysis [4–7].

tually the same if compared with the one extracted from standard MCT analysis (marked by arrows in Fig. 5). Above this temperature, Y is nearly constant, whereas below, Y exhibits a strong temperature dependence.

The question arises why the qualitative picture of MCT is experimentally observed above some temperature whereas the quantitative predictions fail. The systematic variation of $a_{\text{eff}}/a_{\text{MCT}}$ with the degree of fragility (cf. Table I) gives us a key for an understanding of these findings. It was shown in several studies that the fast dynamics include, besides a relaxational contribution, also a contribution due to low-frequency vibrations (the boson peak). Later it was demonstrated that the relative weight of these two contributions correlates with the degree of fragility: the more fragile the system the larger is the relative part of the relaxation in the fast dynamics, and the lower is the corresponding vibrational contribution [16]. The boson peak, which is a significant part of the dynamic spectra of glass formers, is not treated within MCT. Thus one expects deviations at high frequencies due to this boson peak contribution, and these deviations should be stronger for less fragile systems. On the other hand, in the case of colloidal glasses vibrational contributions are not present and this may be the reason why there the MCT predictions are found to hold even quantitatively [17].

Thus from the analysis presented above we can conclude that there is a general scenario for the high temperature dynamics of fragile and strong glass forming liquids: at temperatures higher than some crossover temperature the spectrum of the fast dynamics (including the fast relaxation, the boson peak, etc.) is essentially temperature independent, the α relaxation keeps its spectral form and amplitude unchanged and only its characteristic time scale τ_α varies with T. The recent analysis of B_2O_3 [18] shows that this qualitative picture is valid even for this strong glass former. Our analysis also shows that at some certain crossover temperature this scenario breaks and a qualitative change in dynamics occurs.

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