

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ
ДУБНА

E17-92-519

V.L.Aksenov, E.I.Kornilov, J.Schreiber*

DYNAMICAL RESPONSE FUNCTIONS
FOR THE SCALAR φ^4 -LATTICE MODEL
NEAR FREEZING TEMPERATURE

Submitted to «Journal of Physics: Condensed Matter»

*Institute of Theoretical Physics,
TU Dresden, O-8027 Dresden, Germany

1992

Динамические функции отклика в рамках скалярной решеточной φ^4 -модели вблизи температуры замерзания

Для скалярной решеточной φ^4 -модели структурного фазового перехода в рамках теории связанных мод найдена температура замерзания $T_c^* > T_c$. Для изучения критического поведения этого перехода самосогласованным численным решением уравнений связанных мод получены частотная и температурная зависимости линейной и квадратичной восприимчивостей. Проанализированы два случая: i) идеальная кристаллическая решетка с характерным B -переходом при T_c^* и ii) система со случайно распределенными дефектами и A -переходом при T_c^* . Обсуждаются экспериментальные аспекты представленной теории.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1992

Перевод авторов

Aksenov V.L., Kornilov E.I., Schreiber J.

E17-92-519

Dynamical Response Functions for the Scalar φ^4 -Lattice Model Near Freezing Temperature

For the scalar φ^4 -lattice model of structural phase transitions the freezing transition at a temperature T_c^* above T_c was found in the framework of the mode-coupling theory. To study the critical behaviour of this transition, the frequency and temperature dependencies of the linear and quadratic dynamical susceptibility are investigated by using a self-consistent numerical solution of the mode-coupling equations. Two cases are considered: i) a pure crystalline system with a B -transition at T_c^* and ii) a system with randomly distributed defects with an A -transition at T_c^* . The experimental aspects of the presented results are discussed.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1992

1 Introduction

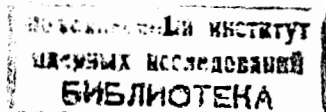
In crystalline systems with a structural phase transition some anomalous behaviour can be observed above the transition temperature T_c (cf. [1, 2]). In perovskites, e.g., the classical soft mode picture of structural phase transitions breaks down and precursor fluctuations give rise to an extra, very narrow central peak in the order parameter fluctuation spectrum (see [3, 2]). In addition to many attempts being made to explain the appearance of correlated clusters (precursors) a concept has been worked out [4, 5], that reminds that for the dynamical glass transition suggested by Götze *et al* [6] on the basis of the mode-coupling theory. According to this theory in pure crystalline systems an ideal, narrow (static) central peak must set in at the so-called freezing temperature T_c^* . This transition is accompanied by an appearance of finite, long-time correlations of the local atomic displacement $u_i = Q_i - \langle Q_i \rangle$, i.e.,

$$L_{i,j} = \lim_{t \rightarrow \infty} \langle u_i(t) u_j(0) \rangle \neq 0 \quad \text{for } T \leq T_c^*, \quad (1)$$

where $\langle \dots \rangle$ denotes the thermodynamic average.

Thus, in the formal sense, the physical situation at $T > T_c$ in the systems with a structural phase transition reminds that in supercooled liquids or polymers above the glass transition point T_g (cf. [7, 8]). In the last years with the mode-coupling theory at hand substantial progress was made in the understanding of the freezing process near the glassy transition. The main result was prediction of the dynamical glass transition temperature $T_c^* \simeq T_g + \Delta T$, where ΔT is about 50K. At this temperature the intensity of the quasistatic central peak in the density fluctuation spectrum and the dynamical density response function exhibit critical scaling behaviour in certain frequency regions [6, 9, 8]. This prediction was partly verified in a number of experiments with glassy materials (see [10, 11, 12, 13, 8, 14]).

Following the idea, it would be interesting to look at $T_c^* > T_c$ for some experimental confirmation of the existence of the freezing transition in crystalline systems, also. Simultaneously the question may arise,



whether in the systems with transitions into structural, dipole, orientational, spin, quadrupole or any other glassy states the dynamic freezing transition can be observed above the thermodynamic glass transition temperature T_g (see [15, 16]). To answer the question investigation of the intensity of the central peak is not sufficient, as some kind of hopping processes could smear the central peak almost at $T \leq T_c^*$, making impossible unambiguous identification. Presence of static or relaxing defects would mask the central peak of intrinsic dynamical origin (cf. [15]). Therefore, the analysis of the dynamical response functions at not too low frequencies is more suitable as the test of the critical scaling behaviour at T_c^* . This has successfully been done for glasses (see [14]).

This paper presents the numerical calculation made in the frame of the mode-coupling theory of the frequency and temperature dependence of the real and imaginary part of the dynamical susceptibility near the freezing transition. The calculation was performed for the scalar φ^4 -lattice model of structural phase transitions. The mode-coupling equations for the isothermal relaxation function were solved directly in the real time space. The resulting integro-differential equation was handled by the predictor-corrector method, and the time evaluation over five time decades was analyzed.

We hope that the presented theoretical results will stimulate detailed experimental search for the freezing transition at temperatures above T_c (or T_g) in crystalline systems. This purpose could serve the neutron and light scattering methods or dielectric and magnetic relaxation measurements.

2 Model and mode-coupling equations

The scalar φ^4 -lattice model is determined by the Hamiltonian

$$H = \sum_i \left(\frac{P_i^2}{2} - \frac{A_i}{2} Q_i^2 + \frac{B_i}{4} Q_i^4 \right) + \frac{1}{4} \sum_{ij} C_{ij} (Q_i - Q_j)^4, \quad (2)$$

where Q_i is the coordinate of the local normal mode that determines the structural phase transition. Within elementary cell the Q_i can be considered as the coordinate of the effective particle of mass $m = 1$, moving in a double-well potential. P_i is then the conjugate momentum of this particle. The interaction between the particles occupying different lattice cells of a 3-dimensional lattice ($i = 1, \dots, N$) is then described by the harmonic force constants C_{ij} . In the pure crystalline case the parameters of the Hamiltonian are independent of the cell-number, but in quenched disordered systems they can be random. To study the influence of defects on the phase transition, only the parameters A_i are assumed to be site-random ($B_i = B$). Following [5] let us consider $A_i = A_D \geq 0$ at defect sites and $A_i = A > 0$, otherwise. If p is the defect concentration, then the probability distribution of A_i looks as

$$P(A_i) = p\delta(A_i - A_D) + (1 - p)\delta(A_i - A). \quad (3)$$

To study the relaxation processes in the model we introduce the averaged isothermal relaxation function

$$\Phi_{lk}(t) = (u_l(t)|u_k) = \int_0^\beta d\beta' \overline{\langle u_l(t - i\beta')u_k \rangle}, \quad \beta = 1/k_B T, \quad (4)$$

where $u_i(t) = Q_i(t) - \langle Q_i \rangle$ is the displacement operator and the bar denotes the configurational average over the random quantities A_i . The initial value of $\Phi_{lk}(t)$ determines the static isothermal susceptibility $\chi_{lk}^T = \Phi_{lk}(t = 0)$. By introducing the Laplace transform of $\Phi_{lk}(t)$ in the form

$$\Phi_{lk}(z) = i \int_0^\infty dt e^{izt} \Phi_{lk}(t) \equiv ((u_l|u_k)), \quad \text{Im}z > 0, \quad (5)$$

the following exact \mathbf{q} -representation can be derived by the equation of motion and using the Mori-projection formalism

$$\Phi_q(z) = -\chi_q^T \left(z - \frac{1/\chi_q^T}{z + M_q(z)} \right)^{-1}, \quad (6)$$

where $\Phi_{lk}(z) = (1/N) \sum_q \Phi_q(z) \exp[iq(R_l - R_k)]$. The relaxation kernel $M_{lk}(z)$ is given by

$$M_{lk}(z) = ((\bar{Q}_l | \bar{Q}_k))_{(2)}, \quad (7)$$

where the lower index (2) denotes the projection procedure to be done in the way suggested by Tserkovnikov [17, 4]. In the spirit of the mode-coupling approximation the relaxation kernel is estimated with the expression that comes from factorization of u_i -powers and truncation of the configurational average in (7) as in [5]. For the classical limit ($\Phi_{lk}(t) \Rightarrow \beta < u_l(t)u_k(0) >$) we get:

$$M_{lk}(t) = v_1 \Phi_{lk}(t) + v_3 \Phi_{lk}^3(t). \quad (8)$$

The coupling parameters are determined in the following way

$$v_1 = A^2 p(1-p)(1 - A_D/A)^2 \quad \text{and} \quad v_3 = 6B^2 k_B^2 T^2. \quad (9)$$

To get considerable values for v_1 even for small concentrations p , strong harmonic defects ($|A_D| \gg A$) are necessary.

For the simplicity of further calculations we exploit the fact that the critical scaling law does not essentially depend on relaxation function dispersion (see [18, 8]). Therefore, to qualitatively investigate the freezing dynamics picture at T_c^* we neglect the relaxation kernel dispersion, i.e., $M_{lk}(t) \approx \delta_{lk}M(t)$. Then, self-consistent determination of a diagonal or local part of the relaxation function becomes possible, if we use the following Ansatz for the isothermal susceptibility:

$$\chi^T = \chi_{ll}^T = \frac{1}{N} \sum_q \chi_q^T = \frac{1}{\omega_0^2}, \quad (10)$$

where ω_0^2 has the form

$$\omega_0^2 = A\tau + C, \quad \tau = (T - T_c)/T_c, \quad (11)$$

and $C = \sum_j C_{ij}$. The Ansatz (10) is in accord with the Landau-theory and will be a reasonable approximation inside the non-critical region with respect to the structural phase transition. Within this approach the critical temperature can be estimated as $T_c = \frac{4}{3}T_0$ (see [5]), where

$f_0 = C/A$ is the dimensionless coupling parameter and $T_0 = A^2/Bk_B$ is some unit of temperature expressed through model parameters. Then we assume that τ_c^* lies outside the critical fluctuation region, as the mode-coupling theory for the freezing transition (also for the dynamical glass transition) assumes no critical fluctuations at T_c (cf. [4, 8]).

It is worth emphasizing that in spite of (10), we do not consider the case of an infinite interaction radius, i.e., $C_{ij} = C/N$. Then the model is solvable and as is shown in [19], at $C/A < 1$ the quantity $L_{ii}(T)$ tends to zero only if $T \rightarrow \infty$, and at $C/A > 1$ vanishes at all. Of course, the freezing transition is expected only for the systems with a finite interaction radius (cf. [20, 21]). The approximation used above should be considered as the approximation valid for the systems, where the freezing transition really exists. Within our theory we cannot prove existence of such a transition. However, if this transition exists, the presented mode-coupling theory may give a good guide line for the experimentalists in the sense the mean field theory does in the case of usual phase transitions.

Thus it is possible to rewrite the equation (6) in the time representation. On carrying out Laplace back transformation of (6) and taking into account the definitions (8—11) one can obtain the following equation:

$$\ddot{\Phi}(t) + \omega_0^2 \Phi(t) + \int_0^t d\tilde{t} \dot{\Phi}(t - \tilde{t}) M(\tilde{t}) = 0, \quad (12)$$

with the initial conditions

$$\Phi(0) = \chi^T, \quad \dot{\Phi}(0) = 0. \quad (13)$$

It is convenient to express (12) through dimensionless variables and parameters. With the new function $D(t) = \Phi(t)/\chi^T$ introduced, it takes the form

$$\ddot{D}(t) + \omega_0^2 D(t) + \int_0^t d\tilde{t} \dot{D}(t - \tilde{t}) M(\tilde{t}) = 0, \quad (14)$$

with the initial conditions

$$D(0) = 1, \quad \dot{D}(0) = 0. \quad (15)$$

For the sake of convenience in following we will also use the dimensionless frequency and time variables, i.e. $\omega \rightarrow \omega/A^{1/2}$ and $t \rightarrow tA^{1/2}$. Within this notation we have now $\omega_0^2 = \tau + f_0$ now.

If no direct measurement of linear susceptibility is possible, then the observed quantities, like damping and velocity of ultrasonic waves, have contributions from several non-linear response functions. To follow the influence of these contributions let us consider the quadratic susceptibility:

$$\chi_{(2)}(\omega) = \omega LT[(u_i^2(t)|u_i^2(0))], \quad (16)$$

where $LT[F(t)]$ means the Laplace transform of $F(t)$. To estimate (16) the factorization procedure used for the approximation of the relaxation kernel can be employed. Neglecting a contribution of the correlation functions of the type of $((u_i^2|u_i))$ and $((u_i^2|\dot{u}_i))$ to $((u_i^2|u_i^2))$, the latter can be approximated by $((u_i^2|u_i^2))_{(2)}$, and then the quadratic susceptibility can be presented in the following way:

$$\chi_{(2)}(\omega) = -\frac{1}{2\pi} \int d\bar{\omega} \frac{e^{\beta\bar{\omega}} - 1}{\omega - \bar{\omega}} \int dt e^{-i\bar{\omega}t} 2 \langle u(t)u \rangle^2 \quad (17)$$

To solve the above equations one needs to apply an appropriate numerical procedure. In the next section we describe the method we suggest for the solution of the integro-differential equations like (14).

3 The numerical procedure

Let us consider the general form of the memory integro-differential equation of the second order. With the new abbreviation $m(t) \equiv M(t)/\omega_0^2$ and adding small phenomenological microscopic relaxation term one obtains the relaxation equation in the following form

$$\ddot{D}(t) + \nu \dot{D}(t) + \omega_0^2 D(t) + \omega_0^2 \int_0^t d\tilde{t} \dot{D}(t - \tilde{t}) m(\tilde{t}) = 0, \quad (18)$$

with the initial conditions

$$D(0) = 1, \quad \dot{D}(0) = 0. \quad (19)$$

The memory-type equations like (12) and (18) appear in numerous theoretical studies of dynamic phenomena. For instance, the theory of long-time relaxation processes in supercooled liquids [8] bases mostly on the analysis of the behavior of the solutions of these integro-differential equations. The specific behavior of the dynamic response functions can be described by solving (18) with an appropriately chosen kernel $m(t)$ as the polynomial in $D(t)$:

$$m(t) = \mathcal{F}\{D(t)\} = \sum_n \tilde{v}_n D^n(t). \quad (20)$$

Comparing to (8) the parameters \tilde{v}_n are given for the scalar φ^4 -lattice model by the following equations

$$\begin{aligned} \tilde{v}_1 &= v_1/\omega_0^4 = (\tau + f_0)^2 p(1-p)(1 - A_D/A)^2, \\ \tilde{v}_3 &= v_3/\omega_0^8 = (\tau + f_0)^4 (T/T_0)^2, \\ \tilde{v}_2 &= \tilde{v}_{n \geq 4} = 0. \end{aligned}$$

The widely used method[8] for solving (18) can be briefly described as follows:

- 1) the attempt function $D^{[0]}(t)$ is taken inside some appropriate time domain,
- 2) the relaxation kernel $m^{[k]}(t) = \mathcal{F}\{D^{[k]}(t)\}$ is calculated (with $k = 0$ in the first step),
- 3) the Laplace transforms of both the correlator $D^{[k]}(z) = LT\{D^{[k]}(t)\}$ and the relaxation kernel $m^{[k]}(z) = LT\{m^{[k]}(t)\}$ are performed,
- 4) the next approximation for the correlator $D^{[k+1]}(z)$ is obtained according to the equation (6)

$$D^{[k+1]}(z) = -\left(z - \frac{\omega_0^2}{z + i\nu + \omega_0^2 m^{[k]}(z)}\right)^{-1}, \quad (21)$$

- 5) the back Laplace transform (BLT) is used for obtaining the approximate solution $D^{[k+1]}(t) = BLT\{D^{[k+1]}(z)\}$, and
- 6) the integral convergence criterion is used to decide on whether stop the iteration procedure or continue calculation from step 2).

However in the own words of the authors[22] "this procedure is not practical ... since Laplace transforms are very cumbersome for functions, which are structured and stretched on such large windows ...". In the present paper we suggest a different numerical approach to the solution of the equation (18). This method in the theory of ordinary differential equations got the name of the predictor-corrector method. The method consists in doing the following subsequent steps.

First, we obtain the Taylor expansion of the unknown function near $t = 0$ up to the seventh order in t

$$D(t) = 1 + a_2 t^2 + a_3 t^3 + \dots + a_7 t^7 \quad (22)$$

in order to explore this precise series in finding solution at the first few steps of the integration scheme. The coefficients a_k are determined after substituting the expansion (22) into (18). The initial conditions were already used in (22).

Application of the predictor-corrector method to the integro-differential equation of the second order means the splitting of the original equation into a system of two first order equations by introducing the new function $P(t) = \dot{D}(t)$. Then we can write the system in the following "standard" form.

$$\dot{P}(t) = F\{D(t), P(t)\}, \quad \dot{D}(t) = G\{D(t), P(t)\}, \quad (23)$$

with the initial conditions $P(0) = 0, D(0) = 1$. Here we introduce

$$F\{D(t), P(t)\} = -\nu P(t) - \omega_0^2(D(t) + I(t)),$$

$$G\{D(t), P(t)\} = P(t),$$

where the integral part is

$$I(t) = \int_0^t d\tilde{t} P(\tilde{t}) m(t - \tilde{t}), \quad (24)$$

with $m(t)$ defined by (20). Then we introduce the grid representation of all functions in the form $D_i = D(t_i), P_i = P(t_i), m_i = m(t_i)$, with

a discrete time $t_i = ih$ expressed through stepsize h . To predict the values of D_{i+1} and P_{i+1} we use

$$P_{i+1}^{(0)} = P_{i-1} + 2hF\{D_i, P_i\}, \quad (25)$$

$$D_{i+1}^{(0)} = D_{i-1} + 2hG\{D_i, P_i\}. \quad (26)$$

and make corrections according to iteration over k

$$P_{i+1}^{(k+1)} = P_i + \frac{h}{2}(F\{D_i, P_i\} + F\{D_{i+1}^{(k)}, P_{i+1}^{(k)}\}), \quad (27)$$

$$D_{i+1}^{(k+1)} = D_i + \frac{h}{2}(G\{D_i, P_i\} + G\{D_{i+1}^{(k)}, P_{i+1}^{(k)}\}), \quad (28)$$

while the convergence criterion $\sqrt{(D_{i+1}^{(k+1)} - D_{i+1}^{(k)})^2 + (P_{i+1}^{(k+1)} - P_{i+1}^{(k)})^2} \leq \epsilon$ is satisfied. One of the advantages of the predictor-corrector method that consists in a more exact calculation of the correlation function $D(t)$ near the beginning of the t -axis is due to the use of this very point convergence criterion. Then we take into account a simple estimate of the discretization error of the predictor-corrector method[23] by

$$\delta P_{i+1} = \frac{1}{5}(P_{i+1}^{(0)} - P_{i+1}^{(k+1)}), \quad \delta D_{i+1} = \frac{1}{5}(D_{i+1}^{(0)} - D_{i+1}^{(k+1)}), \quad (29)$$

and use (29) to obtain the final correction for the solution (27-28).

It is necessary to say a few words about the calculation of the integral part $I(t)$. Choosing a scheme of numerical integration it is necessary to take into account the complex estimate of calculation laboriousness. On one hand, there exist many numerical methods of enhanced precision (h^3 or higher order). But, all of them require larger volume calculations with increasing accuracy. On the other hand, to find solutions in every new time point t_i , it is necessary to recalculate (24). Since usually we need about $10^3 - 10^4$ points in a time domain, it appears suitable to use the simplest scheme of the first order in h :

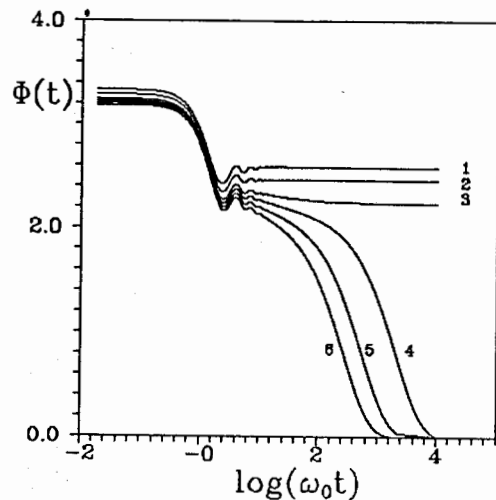


Figure 1: The time dependence of the relaxation function $\Phi(t)$ of the F_3 -model for different temperatures τ : 1 — 0; 2 — 0.004; 3 — 0.008; 4 — 0.010; 5 — 0.012; 6 — 0.014. The freezing temperature $\tau_c^* \approx 0.0083$ for this set of model parameters.

$$I_i = \frac{h}{2}(P_0 m_i + P_i m_0) + h \sum_{j=1}^{i-1} P_j m_{i-j}. \quad (30)$$

This notation illustrates another advantage of this scheme. Namely, in the stage of making the correction iteration the sum is calculated only once.

And, finally, once the dimensionless solution $D(t)$ within a suitable time domain is obtained, we renormalize it to operate in the following with the mode coupling correlator $\Phi(t)$. This transformation is the reverse one to that we used for deriving (14) from (12). Further numerics are sooner standard than new. Thus, for example, we performed Laplace transform of the correlators by the Filon algorithm[24].

4 Results and discussion

The time dependent local relaxation function $\Phi(t)$ from (12) is shown in figure 1 for the case: $v_1 = 0$ ($p = 0$) — (F_3 -model in Götze notations [8]), $f_0 = 0.3$, and $T_c = 0.1T_0$. Over nearly six decades time evaluation can be followed. Since $\tau < \tau_c^* \approx 0.0083$, the function $\Phi(t)$ has a finite value for $t \rightarrow \infty$ in agreement with the result directly obtained from (6), if one takes the limit $L_{ii} = \lim_{z \rightarrow i0} z \Phi_{ii}(z)$ (cf. [5]). The value $l_c^* = L_{ii}(\tau_c^*)/\chi^T(\tau_c^*) = \frac{2}{3}$ (a discrete B-transition [8]). For $\tau > \tau_c^*$ two characteristic relaxation regions can be distinguished: when $\Phi(t) \sim 2.0$ then it is the β -relaxation and the region when $\Phi(t) \rightarrow 0$ belongs to α -relaxation. To have more information about both relaxation regions the Laplace transform of $\Phi(t)$ should be studied. In figures 2 and 3 the real and imaginary part of the dynamic susceptibility

$$\chi(\omega) = \omega LT[\Phi(t)](\omega) \quad (31)$$

for the F_3 -model are shown. It can be seen that the linear and quadratic susceptibility have nearly same qualitative ω - and T -dependencies. From these curves qualitative representation of the scaling laws of α - ($\omega \sim 10^{-3}$) and β -relaxation ($\omega \sim 10^{-1}$) can be derived. Götze [25, 8] found the analytical expressions for these scaling laws from the equations (6) and (8) using $\epsilon = (T - T_c^*)/T_c^*$, as the small expansion parameter, and considering the $\omega \rightarrow 0$ limit. For $\epsilon > 0$ two frequency scales $\omega_\alpha \sim \epsilon^{-1/2a+1/2b}$ and $\omega_\beta \sim \epsilon^{1/2a}$ separate the α - and β -relaxation. Around ω_β the simple interpolation formula

$$\chi''(\omega) \approx \sqrt{\epsilon} [\Gamma(1-a) \sin(\pi a/2) (\omega/\omega_\beta)^a + B \Gamma(1+b) \sin(\pi b/2) (\omega_\beta/\omega)^b] \quad (32)$$

can give a good approximation to the susceptibility behaviour illustrated in figure 2. Differently from the usual phase transition case the exponent parameters a and b are not the universal ones and depend on model parameters and, hence, on temperature. According to [25] these parameters are determined by the equation

$$\Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b) = \lambda(T), \quad (33)$$

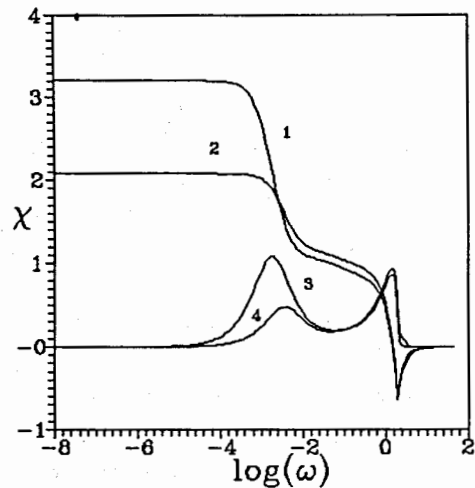


Figure 2: The frequency dependence of the real (1 — χ' and 2 — $\chi'_{(2)}$) and imaginary (3 — χ'' and 4 — $\chi''_{(2)}$) part of the susceptibility of the F_3 -model for the temperature $\tau = 0.012 > \tau_c^*$. The odd and even labels correspond to a linear and quadratic part of the susceptibility, respectively. See text for details.

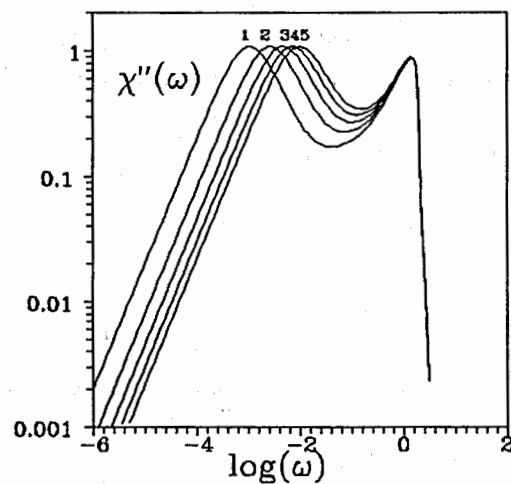


Figure 3: The imaginary part of susceptibility $\chi''(\omega)$ of the F_3 -model versus $\log(\omega)$ for different temperatures τ : 1 — 0.011, 2 — 0.013, 3 — 0.015, 4 — 0.017, 5 — 0.019.

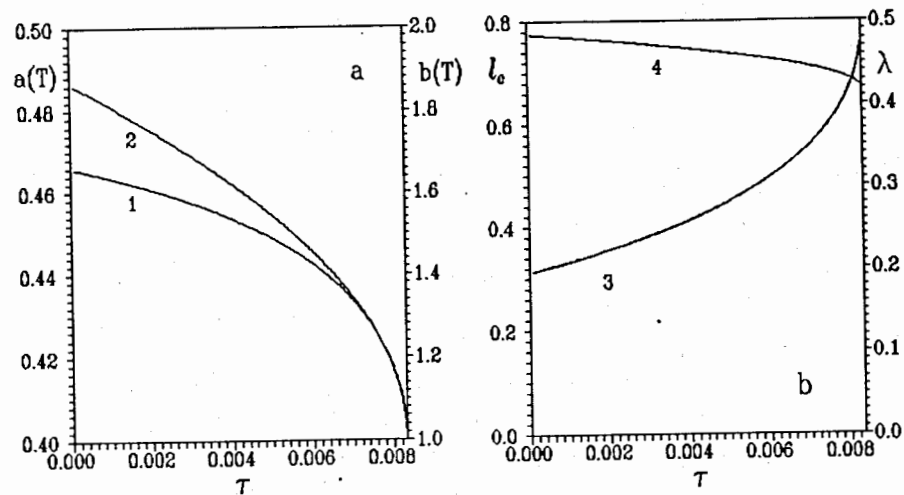


Figure 4: (a) The characteristic exponents a (1) and b (2), and (b) the exponent parameter λ (3), and the nonergodic constant l_c (4), versus temperature for the F_3 -model.

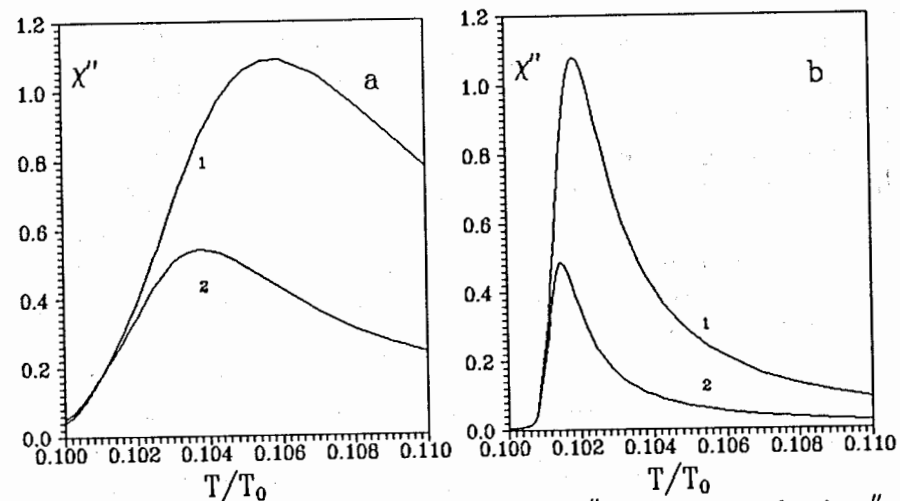


Figure 5: The imaginary part of the linear χ'' (1) and quadratic $\chi''_{(2)}$ (2) susceptibility versus temperature for the F_3 -model for $\omega = 0.1$ (a) and $\omega = 0.01$ (b). The model parameters are $T_c = 0.1T_0$ and $\tau_c^* \approx 0.0083$.

where $\Gamma(x)$ is the Gamma-function. The exponent parameter $\lambda(T)$ is given by

$$\lambda(T) = 3(1 - l_c)^3 v_3 l_c, \quad l_c = \beta L_{ii}(T)/\chi^T(T). \quad (34)$$

In figure 4 the quantities $l_c(T)$, $\lambda(T)$, $a(T)$ and $b(T)$ are shown as the functions of temperature.

Another insight into scaling behaviour one can have by considering the temperature dependence of $\chi'(\omega, T)$ and $\chi''(\omega, T)$ at fixed frequency ω . This is the typical experimental situation, e.g., with Brillouin scattering. The corresponding results are plotted in figure 5. Unfortunately, these curves show that the T -dependence of $\chi(\omega, T)$ lacks sensitivity for the experimentalists to detect anomalous critical behaviour at T_c^* . For $\epsilon < 0$, e.g., $\chi''(\omega, T) \sim \omega|\epsilon|^{-1/(2a)+1/2}$ was predicted by the theory. One has to remember also, that T_c^* is very close to T_c in the pure B-type transition case (cf. [4, 5]) and no definite conclusion about the freezing transition in pure systems can be drawn from such experiments.

Let us now consider the F_{13} -model ($v_1 \neq 0$), arising, when one includes into consideration the nonzero defect concentration $p \neq 0$. To enlarge the interval between T_c and T_c^* we take $v_1 = 6.25A^2$ and $f_0 = 2.1$, that correspond to $T_c = 0.7T_0$ and $T_c^* = 0.98T_0$ or $\tau_c^* = 0.4$. As we choose the control parameter v_1 large enough the freezing transition changes its type, i.e. now $L_{ii}(\tau \rightarrow \tau_c^*) \rightarrow \epsilon \rightarrow 0$ (the A-transition [8]). Due to this continuous transition no freezing of α -peak occurs, as shown in figure 6. There is no α -peak at all. The scaling behaviour is now restricted to β -like relaxation at $\omega \sim \omega_\beta \sim \epsilon^{1/a'}$: $\chi''(\omega) \sim \omega\epsilon^{1-1/a'}$ for $\omega \ll \omega_\beta$ and $\chi''(\omega) \sim \omega^{a'}$ for $\omega \gg \omega_\beta$. The temperature dependence of the parameter a' is shown in figure 7. (see (33)). From the double logarithmic plot of $\chi''(\omega)$ in figure 6 it follows that the analytical scaling laws are not quite illustrative in such a presentation. On the other hand the critical temperature behaviour of $\chi''(\omega, \tau)$ at fixed frequency is clearly seen in a relatively wide frequency window (see figure 8). For rather different frequencies $\chi''(\omega, \tau)$ has a pronounced peak at τ_c^* . The peak becomes the broader the higher is the frequency. Nevertheless, for $T < T_p^-$ and $T > T_p^+$, where T_p is determined by $\omega = \omega_\beta(T_p)$, the

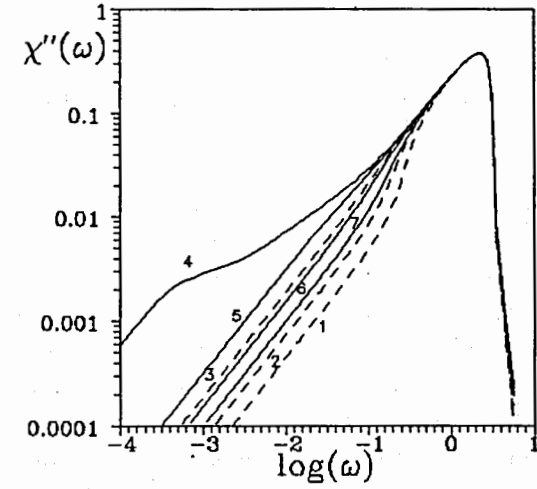


Figure 6: The imaginary part of the susceptibility $\chi''(\omega)$ of the F_{13} -model versus $\log(\omega)$ for different temperatures τ : 1 — 0; 2 — 0.10; 3 — 0.25; 4 — 0.40; 5 — 0.50; 6 — 0.60; 7 — 0.70. Dashed lines correspond to a nonergodic regime, whereas solid lines correspond to the temperatures $\tau \geq \tau_c^* = 0.40$.

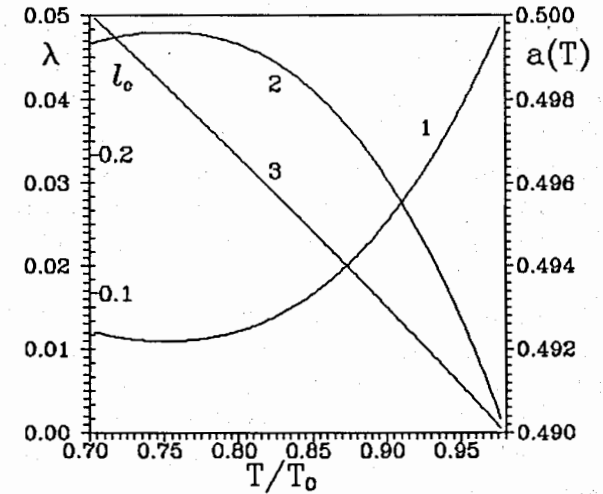


Figure 7: The characteristic exponent a (1), the exponent parameter λ (2), and the nonergodic constant l_c (3) versus temperature for the F_{13} -model.

scaling law $\chi''(\omega, T)/\omega \sim \epsilon^{-1/a'+1}$ can be sufficiently well recognized, if the measuring frequency is not too high (see figure 9). Here the influence of the quadratic susceptibility $\chi_{(2)}(\omega)$ is not drastic and in the region of the scaling law validity ($T < T_p^-$ and $T > T_p^+$) $\chi_{(2)}''(\omega, T)$ is a nearly flat function of temperature. Therefore, the critical behaviour in $\chi''(\omega, T)$ is not masked with quadratic susceptibility, if the measured quantity is influenced by both susceptibilities.

At the same time as $\chi''(\omega, T)$ shows a peak at τ_c^* the real part $\chi'(\omega, T)$ changes its slope at τ_c^* and a cusp-like behaviour is observed the better the lower is the frequency, up to $\omega \rightarrow 0$ (see figure 8). This feature of the A-type freezing transition reminds of the spin-glass transition. However, unlike that transition the freezing temperature τ_c^* does not depend on the measuring frequency. The important point to be decided on is whether the experimentally found anomalies (the cusp-behaviour) are connected with the dynamical freezing transition or with the thermodynamic glass transition.

There were made several attempts to describe the transitions in spin-glasses [26], in orientational glasses [27], and in polymers [28] in the frame of the mode-coupling theory. This possibility has to be ruled out in the light of our results for the A-type freezing transition. This means that all peaks in loss functions or the cusp-like points in real parts of the susceptibility suffering a clear frequency shift (e.g., by an Arrhenius or Vogel-Fulcher law) cannot be ascribed to a dynamical freezing transition found by the mode-coupling theory. These anomalies are caused by some other type of the freezing kinetics, e.g., due to relaxation in a random potential landscape (cf. [29, 30]).

We wish to emphasize again, that, as far as it concerns the application of our results obtained in the frame of the mode-coupling approach, we look for the new kind of the freezing transition, which should take place above T_c in the systems with usual structural phase transitions. For the systems with a structural glass transition this dynamical transition should be searched for above the frequency dependent thermodynamical glass transition point T_g . But it is possible that this transition is not observable because of too strong influence of the relaxing defects

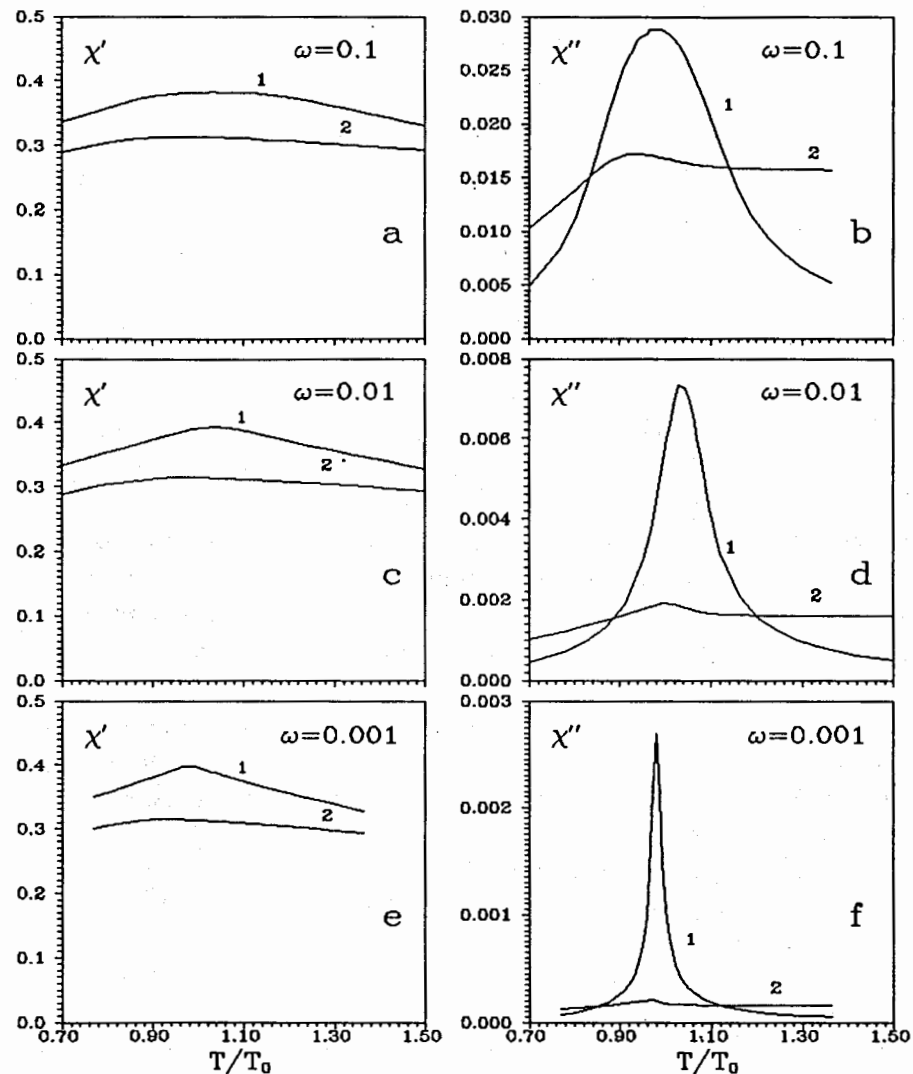


Figure 8: The temperature dependence of the real χ' (a,c,e) and imaginary χ'' (b,d,f) parts of the susceptibility of the F_{13} -model for the frequencies $\omega = 0.1, 0.01, 0.001$. The labels 1 and 2 correspond to the linear and quadratic parts of susceptibility, respectively.

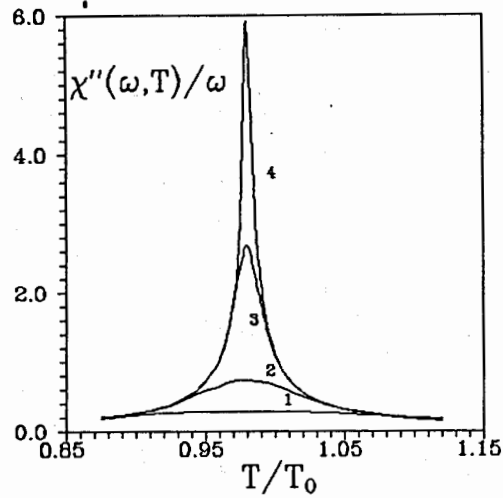


Figure 9: An illustration of a tendency to reach the master function for the imaginary part of susceptibility with a decrease of frequency. Here ω is: 1 — 0.1; 2 — 0.01; 3 — 0.001; 4 — 0.0001; and for the higher frequencies the curves coincide with the latter case.

or hopping processes connected with correlated clusters. These effects are neglected in the mode-coupling theory (cf. [31, 32, 8]). In principle there are two ways of overcoming these shortcomings of the presented theory.

i) Following the phenomenological approach of [15] the relaxing defects can be included via Ansatz (cf. eq. (6)).

$$M_{lk}(z) = \frac{\Delta_l}{iz\tau_l + 1} + M_{lk}^o(z), \quad (35)$$

where $M_{lk}^o(z)$ is determined by eq. (8). In the general case the parameter Δ_l and the relaxation time (e.g., $\tau_l = \tau_l^o \exp(-E_a/k_B T)$) of a local relaxing defect are the random quantities. This additional relaxation process yields an α -like loss peak also at $T < T_c^*$ and can modify $\chi'(\omega, T)$ and $\chi''(\omega, T)$. For instance the loss peak at T_c^* can be remarkably asymmetric (see [15]).

ii) According to the generalized kinetic equation approach of [33, 32] hopping processes can be incorporated into by an improved expression

for the relaxation kernel (7)

$$M_{\mathbf{q}}(z) = M_{\mathbf{q}}^o(z)/(1 - \delta_{\mathbf{q}}(z)M_{\mathbf{q}}^o(z)), \quad (36)$$

where the new kernel $\delta_{\mathbf{q}}(z)$ contains the correlation functions of the type $(\dot{u}_l(t)|\dot{u}_k(0))$ ($\delta_{\mathbf{q}}(z \rightarrow 0) \sim z$). In consequence of this relaxation process the ideal central peak is smeared, i.e., at $T < T_c^*$ the α -like relaxation peak remains in $\chi''(\omega, T)$. This peak, however, does not show any critical scaling behaviour, as happens for the systems with a broad distribution of relaxation times.

Hence under certain but not yet very clear circumstances the typical scaling dynamics of the freezing transition can be masked and the critical scaling behaviour of α -relaxation be not observable at all. In spite of that the critical β -relaxation should be seen in the systems, where the time constants of the hopping processes are large enough in comparison with the characteristic time scale $1/\omega_{\beta}$ of β -relaxation. Therefore, the chance of finding a dynamical freezing transition increases, if the measuring frequency is taken sufficiently high, but not too high.

So far a clear indication that the freezing transition would take place was observed only for supercooled liquids and polymers above T_g (see [8, 14]). On the other hand interesting data were obtained for a plastic crystal of Difluortetrachlorethane (DFTCE). Using the Brillouin scattering technique ($\omega \sim 1 - 10 \text{ GHz}$) Krüger *et al* [34, 35] detected a frequency independent maximum in the damping $\Gamma(\omega, T)$ of longitudinal acoustic phonons and a first hint to the scaling behaviour $\Gamma(\omega, T) \sim (T - T_c^*)^{-\nu}$ for $T < T_c^* \approx 160 - 170 \text{ K}$. Furthermore, the longitudinal sound velocity changed its slope at T_c^* . Assuming a linear coupling of the order parameter and elastic degrees of freedom in this plastic crystal, a change in eigenfrequencies ($\omega_{q,L}^2 = C_L q^2$) and damping, $\Gamma(\omega, T)$, of longitudinal acoustic phonons can be determined via dynamical susceptibility as follows:

$$\Delta C_L(T) \sim \chi'(\omega_{q,L}, T) \quad \text{and} \quad \Delta \Gamma(\omega, T) \sim \chi''(\omega, T). \quad (37)$$

On the basis of these relations the Brillouin scattering results for DFTCE can be interpreted in the framework of the A-type freezing transition discussed above. In this connection it is worth noting that the DFTCE possesses a real glass transition at $T_g = 90K$, where the sound velocity experiences a cusp-like change and the specific heat has nearly a jump.

However, it is early to make any final conclusions about this system. The experimental data must be carefully verified and a detailed analysis in terms of the mode-coupling theory has to be made. These are the plans for the future.

We finalize this section with a remark on the attempts made to explain the central peak phenomenon by defect induced condensation. In [36] a theory was elaborated for unstable lattices with a finite concentration n of defects. This theory predicts a defect induced phase transition at $T_c(n) > T_c(\text{pure})$, where the order parameter becomes substantially non-zero only at defect sites, but at $T \leq T_c(\text{pure})$ the whole system becomes long range ordered. Interesting T , q and ω dependencies of the central component of the order parameter fluctuation spectrum were found. A striking difference from our theory is connected with the anomalous critical behaviour of the static susceptibility at $T_c(n)$. The mode-coupling theory for the dynamical freezing transition does not predict any anomalies in isothermal static susceptibility and only a cusp is allowed for the static limit of the dynamical response function. Therefore, a simple criterion can be used to distinguish between the dynamical freezing mechanism of the mode-coupling theory and the defect induced condensation, proposed by Schwabl and Täuber [36]. To our knowledge the data on the static susceptibility for systems with a structural phase transition contain no indication of any remarkable anomalies above T_c . Therefore, we hope that the dynamical freezing transition is to be observed in these systems, also.

5 Conclusions

The presented results of the numerical investigations of the ω - and T -dependence of the dynamical response function near T_c^* within the scalar φ^4 -lattice model offers some suitable possibility for the experimental confirmation of the existence of the freezing transition above the temperature of the structural phase transition. The used mode-coupling approach predicts either *i*) a B-type transition in pure systems, where an α -relaxation peak freezes in at T_c^* or *ii*) an A-type transition for the systems with strong enough defects, where the central peak begins to appear with zero intensity. It seems that the possibility of experimental observation appears more realistic in the latter case.

To the best of our knowledge the experimental data on the intensity of the central peak do not contain any direct information about the transition region $T \sim T_c^*$ (cf. [3, 2, 37]). A crude estimate of the central peak intensity always points to the A-type transition, if any freezing transition exists at all. The examples are the compounds SrTiO_3 [38, 3, 2], RbCaF_4 [39, 3], and the TSCC [40, 41, 37] samples.

In case of a B-type freezing transition the temperature T_c^* lies very near the phase transition point T_c . Therefore, the critical fluctuations certainly mask the anomalous fluctuations that belong to the freezing transition. Nevertheless, a careful study of the ω -dependence of the order parameter susceptibility at temperatures $T > T_c$ might provide some hint of the freezing transition occurrence. And especially, the existence of the scaling behaviour of two types around the α - and β -transition would give a strong indication of the new phenomenon taking place, though the mode-coupling theory could be too crude to correctly describe the scaling exponents (cf. [21]).

In case of an A-transition the situation is more favorable for carrying out an experimental test. Here, the temperature T_c^* lies far from T_c . So the critical fluctuations can be excluded. Then the T -dependence of the dynamical response function for the reasonably high measuring frequency ω must reveal some peculiarities characteristic of the A-type

freezing transition as such transition occurs. The key point is the ω -independent loss-peak (or susceptibility-cusp) at a sought for temperature T_c^* , as well as the characteristic behaviour of the loss-peak wing.

Besides direct measurements of the order parameter susceptibility (mechanic, dielectric, or magnetic) indirect ones appear also very useful for the solution of the considered problem. First of all we think about the neutron- and Brillouin-scattering investigations (see [10, 11, 14, 42]). The other methods, like ultrasonic and NMR measurements also offer the ways of detecting anomalies of the above considered kind at freezing transition. A very good candidate to be used in the investigation of a freezing transition at $T_c^* > T_c$ is the TSCC compound (cf. [40, 41, 37]). TSCC is a strongly anisotropic system with a one-component order parameter, i.e., this system can be well described by the scalar φ^4 -lattice model of structural phase transitions. In fact in TSCC the central peak was found above T_c in the temperature range $T_c < T < T_c^* = T_c + \Delta T^*$, where $\Delta T^* \simeq 20K$. Investigation of the ω - and T -dependence of the dynamical scattering function for this system, as was done for $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ by Cummins *et al* [14], would be very interesting. A corresponding consideration of the other systems with structural instability, especially of perovskites, would be also very desirable. In this connection it cannot be excluded, that the recently found anomalies in dielectric [43], EPR [44] and neutron scattering [45] measurements on SrTiO_3 at $T_0 \simeq 40K$ will be related to the dynamical freezing transition of the above discussed kind. Of course, in this case the quantum corrections have to be incorporated into some adequate theory (cf. [46]). As the result one may hope to find the answer to the still open question of the existence of the freezing transition in crystalline systems with structural phase transitions.

At that one should keep in mind the following circumstances. The dynamical scattering function is determined by the density-density correlation functions and can be approximated by the order parameter correlation function only in the lowest order. Therefore, it is necessary to include in the mode-coupling theory the higher order fluctuation contributions. In principle it is possible, that the freezing transition can

be observed only due to these contributions (cf. [8]). Now we deal with some theoretical approaches to this question.

As is mentioned in Chapter 4 it would be also of interest to reanalyze the experimental data obtained for crystalline or disordered systems showing a glass-like transition at the temperature T_g . An intriguing question is whether a dynamical freezing transition occurs above the thermodynamic glass transition in such systems, also. The findings for DFTCE [34] are therefore of great importance and hence a detailed analysis of all available experimental data for DFTCE is very desirable. It would be important as well to clarify the differences and similarities between the freezing-like transition in DFTCE and in the systems, e.g., with an orientational glass transition (see [15]) and a spin glass transition. It is likely that in the latter case the kinetics in a fixed stochastic energy barrier landscape dominate in the behaviour of the dynamical response function and it might even happen, that no dynamical freezing transition in the above sense takes place.

Finally, we want to point to the problem of clearing up the microscopic structure of the frozen state at temperatures $T_{c(g)} < T < T_{c(g)}^*$. In the above reported numerical treatment only the diagonal part of the relaxation function was taken into account. Exploiting the q -dependent diffuse scattering in the neutron- or X-ray diffraction experiments one can obtain essential information on the correlated cluster formation in the quoted temperature range.

Acknowledgments

The stimulating discussions with Dr J. Baschnagel, Prof W. Götze, Prof R. Schilling and Prof N.M. Plakida are gratefully acknowledged. We thank Dr S. Flach for numerous useful comments. We feel indebted to Dr. J.-K. Krüger for valuable comments on the experimental aspects of the theory. Our thanks are also due to Mrs T. Drozdova for her help in the preparation of the English version of this paper. One of us (E.I.K.)

thanks the "Deutsche Akademischer Austauschdienst (DAAD)" for financial support. The present work was partly supported by the VDI—Technologiezentrum Düsseldorf under project 01170/011.

References

- [1] K.A. Müller. In *Dynamical Critical Phenomena and Related Topics*, page 210. ed C.P. Enz (Berlin, Heidelberg, New York: Springer), 1979.
- [2] K.A. Müller. In *Statics and Dynamics of Nonlinear Systems*, page 68. ed G. Benedek, et. al. (Berlin, Heidelberg, New York: Springer), 1983.
- [3] A.D. Bruce and R.A. Cowley. In *Structural Phase Transitions*. (London: Taylor and Francis), 1981.
- [4] V.L. Aksenov, M. Bobeth, N.M. Plakida, and J. Schreiber. *J. Phys.*, **C20**, 375, 1987.
- [5] V.L. Aksenov, M. Bobeth, N.M. Plakida, and J. Schreiber. *Z. f. Phys.*, **B69**, 393, 1987.
- [6] U. Bengtzelius, W. Götze, and A. Sjölander. *J. Phys. C: Solid State Phys.*, **17**, 5915, 1984.
- [7] C.A. Angell. *J. Phys. Chem. Solids*, **49**, 863, 1988.
- [8] W. Götze. In *Liquids, Freezing and the Glass Transition*, page 289. ed J.P. Hansen, D. Levesque and J. Zinn-Justin (Amsterdam: North-Holland), 1991.
- [9] W. Götze and Sjögren. *J Phys.:Condens. Matter*, **1**, 4183, 1989.
- [10] F. Mezei, W. Knaak, and B. Farago. *Physica Scripta*, **T 19**, 363, 1987.
- [11] D. Richter, ed. *Dynamics of Disordered Materials* (Berlin: Springer), 1989.
- [12] D. Richter, et. al. *Phys. Rev. Lett.*, **24**, 2921, 1990.
- [13] W. Petry, et. al. *Z. Phys.*, **B83**, 175, 1991.
- [14] G. Li, W.M. Du, X.K. Chen, and H.Z. Cummins. *Phys. Rev.*, **A 45**, 3867, 1992.

- [15] C. Bostoen and K.H. Michel. *Phys. Rev.*, **B43**, 4415, 1991.
- [16] W. Petry, et. al. *Phys. Rev.*, **B44**, 210, 1991.
- [17] Yu.A. Tserkovnikov. *Theor. Math. Phys.*, **49**, 219, 1981.
- [18] W. Götze. *Z. Phys.*, **B60**, 195, 1985.
- [19] S. Flach. *Z. Phys.*, **B82**, 419, 1991.
- [20] S. Flach, J. Siewert, R. Siems, and J. Schreiber. *J. Phys. Cond. Matt.*, **3**, 7061, 1991.
- [21] S. Flach and J. Siewert. *J Phys.:Condens. Matter*, **4**, L363, 1992.
- [22] M. Fuchs, W. Götze, I. Hofacker, and A. Latz. *J Phys.:Condens. Matter*, **3**, 5047, 1991.
- [23] D.D. McCracken and W.S. Dorn. *Numerical Methods and FORTRAN Programming*. (John Wiley and Sons, Inc., New York, London, Sydney), 1965.
- [24] M. Abramowitz and I.A. Stegun. *Pocketbook of Mathematical Functions*. (Frankfurt/Main: Harri Deutsch), 1984.
- [25] W. Götze. *Z. Phys.*, **B56**, 139, 1984.
- [26] W. Götze and L. Sjögren. *J. Phys. C: Solid State Phys.*, **17**, 5759, 1984.
- [27] K.H. Michel. *Z. Phys.*, **B68**, 259, 1987.
- [28] L. Sjögren. *J Phys.:Condens. Matter*, **3**, 5023, 1991.
- [29] R.G. Palmer. *Adv. Phys.*, **31**, 669, 1982.
- [30] K. Binder and A.P. Young. *Rev. Mod. Phys.*, **58**, 811, 1986.
- [31] W. Götze and L. Sjögren. *J. Phys. C:Solid State Phys.*, **21**, 3407, 1988.
- [32] L. Sjögren. *Z. Phys.*, **B79**, 5, 1990.
- [33] L. Sjögren and A. Sjölander. *J. Phys.*, **C12**, 4369, 1979.
- [34] J. Schreiber, J.-K. Krüger, R. Jimenez, and J.F. Legrand. *Proceedings of "2nd Meeting on disorder in molecular solids"*, Garchy, 1991.

- [35] J.-K. Krüger. private communication, 1991.
- [36] F. Schwabl and U.C. Täuber. *Phys. Rev.*, B44, 11112, 1991.
- [37] J. Petzelt, et. al. *Sol. Stat. Commun.*, 73, 5, 1990.
- [38] R. Currat, K.A. Müller, W. Berlinger, and F. Denoyer. *Phys. Rev.*, B17, 2937, 1980.
- [39] A. Almairac, M. Rousseau, J.Y. Gesland, J. Nouet, and B. Hennion. *J. Phys., Paris*, 38, 1429, 1977.
- [40] Cz. Pawlaczyk and H.G. Unruh, et. al. *phys. stat. sol. (b)*, 136, 435, 1986.
- [41] J. Petzelt, et. al. *Ferroelectrics*, 80, 829, 1988.
- [42] J.-K. Krüger. In *Optical Techniques to Characterize Polymer Systems*. ed. H. Bässler (Amsterdam: Elsevier Sc. Publ.), 1989.
- [43] M. Maglione, S. Rod, and U.T. Hochli. *Europh. Lett.*, 4, 631, 1987.
- [44] K.A. Müller and W. Berlinguer and E. Tosatti. *Z. Phys.*, B84, 277, 1991.
- [45] R. Vacher, B. Hennion, and K.A. Müller. *Europh. Lett.*, 1992.
- [46] S. Flach and J. Schreiber. *phys. stat. sol. (b)*, 140, K1, 1987.

Received by Publishing Department
on December 10, 1992.