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Long-time correlations in a model of structural phase transitions with infinite range interaction

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The long-time value of the displacement-displacement correlation function is calculated within the ϕ^4-lattice model used to simulate structural phase transitions. Its temperature dependence and dispersion is discussed for infinite range interaction. Special attent is devoted to the natural explanation of a central peak in the scattering function using nonvanishing long-time correlations.

1. Introduction

A number of papers was devoted to the explanation of the phenomenon of a central peak in the scattering function near structural phase transitions outside the critical region [1]. Besides of the possibility of localized vibrations [2] due to defects also a general appearing of long-time values of the displacement-displacement correlation function without defects due to the special nonlinearities (phase separation) was dicussed in [3] to explain the central peak. These long-time correlations are then naturally the source of the central peak and of all other pecularities in the thermodynamics like the freezing-in of the "soft" phonon mode etc. In this case the soft-mode picture of Anderson and Cochran [4, 5] works no more since the divergency of the susceptibility doesn't come from the vanishing (softening) of a temperature dependent phonon frequency because the latter doesn't soften completely. We want to point at the general usefulness of long-time correlations in non-ordered systems as a criterion for the indication of new features as the spin-glass state [6], the liquid-glass transition [7] and particle localization in random potentials [7].

The calculations of the long-time correlations in [3] were done within a mode-coupling approximation for a quantum system with finite range interaction. We solved the corresponding classical problem in the case of infinite range interaction exact. These calculations were prepared by Onodera [8] in the limit of high and low temperatures analytically. We solved this problem in the whole temperature range numerically.

In Sect. 2 the model is introduced and the thermodynamics is calculated (without long-time correlations). In Sect. 3 the long-time correlations including their dispersion are calculated. In Sect. 4 the appearance of a central peak is discussed. Section 5 is devoted to a discussion of the numerical results. A summary is given in Sect. 6.

2. The structural phase transition model

To study SPT we use the scalar ϕ^4-lattice model (see e.g. [9]):

$$H=\sum_l\left(\frac{P_l^2}{2m}-\frac{1}{2}AX_l^2+\frac{1}{4}BX_l^4\right)+\frac{1}{4}\sum_{l,k}C_{lk}(X_l-X_k)^2 \quad (2.1)$$

$$X_l=\sum_q \mathrm{e}^{iql}X_q \qquad P_l=\sum_q \mathrm{e}^{iql}P_q \quad (2.2)$$

X_q and P_q are canonically conjugated phonon normal coordinate and momentum with wave vector q. Index 1 runs over all unit cells, C_{lk} is the harmonical interaction, A and B are the parameters of the local double-well potential. Model (2.1) which belongs to the Ising universality class [9] is the simplest one for obtaining temperature dependent phonon frequencies [9] as it is usually measured in a broad class of perovskite systems [10]. The anharmonicity X^4 in (2.1) guarantees a temperature dependence of the phonon frequencies up to arbitrary high temperatures. A SPT in model (2.1) occurs if $A>0$. The double-well potentials for soft phonons producing a SPT are well established from frozen phonon total energy calculations (see e.g. [11]).

In a first step we introduce dimensionless variables by scaling all variables with A, B and m:

$$H\to\frac{B}{A^2}H, \qquad X\to\sqrt{\frac{B}{A}}X, \qquad P\to\frac{1}{A}\sqrt{\frac{B}{m}}P$$

$$f_{lk}=\frac{C_{lk}}{A}, \qquad T\to\frac{B}{A^2}kT, \qquad t\to\sqrt{\frac{A}{m}}t,$$

$$H=\sum_l\left(\frac{P_l^2}{2}-\frac{1}{2}X_l^2+\frac{1}{4}X_l^4\right)+\frac{1}{4}\sum_{l,k}f_{lk}(X_l-X_k)^2 \quad (2.3)$$

In general no exact solution for this problem is found. Trying to apply Green function technique one has to estimate the corrections due to decoupling procedures [10]. However it is well-known that in the special case of infinite range interaction

$$f_q = f_0 \, e^{-q^2 r_0^2}, \quad r_0 \to \infty \tag{2.4}$$

when each particle interacts with all others

$$f_{lk} = \frac{f_0}{N}, \quad N \equiv \text{number of unit cells} \tag{2.5}$$

model (2.3) reduces to an effective one-particle problem with a mean field [9]:

$$H(P,X) = \frac{P^2}{2} - \frac{1}{2}(1-f_0)X^2 + \frac{1}{4}X^4 - f_0\langle X\rangle X,$$
$$\langle\ldots\rangle = \frac{1}{Z}\int d\Gamma \, e^{-\beta H(P,X)} \ldots, \quad Z = \int d\Gamma \, e^{-\beta H(P,X)},$$
$$d\Gamma = dP \cdot dX, \quad \beta = \frac{1}{T}. \tag{2.6}$$

Onodera [8] investigated the dynamical properties of model (2.6). Especially he mentioned the existence of a nonvanishing d.c. component of the correlation function $F(t)$ for $f_0 < 1$:

$$F(t) = \langle x(t) \cdot x(0)\rangle, \quad x(0) = X, \quad x(t) = x(t, X, P),$$
$$p(0) = P, \quad \lim_{t\to\infty} F(t) \neq 0, \quad f_0 < 1. \tag{2.7}$$

In the presence of these long-time correlations (LTC) the phonon peak in the excitation spectrum does not soften completely as the SPT is reached. However the SPT is of second order giving rise to look for another dynamics in the system producing a divergence in the static susceptibility at T_c. In the next section we will show the LTC at $q=0$ being the reason for this divergence.

From the theory of linear response [12] it follows that the static susceptibility in the $q=0$-point of the Brillouin zone (BZ) is given by [8]

$$\chi^T_{q=0} = \frac{1}{\dfrac{T}{\langle X_l^2\rangle} - f_0}. \tag{2.8}$$

All calculations beginning with (2.8) are done for $T \geqq T_c$ i.e. for $\langle X_l\rangle = 0$. The static susceptibility is defined through the correlation function (2.7):

$$\chi^T_{lk} = \beta\langle X_l X_k\rangle. \tag{2.9}$$

In our case of long-range interaction we get q-independent values of the susceptibility $\left(\langle X_l X_k\rangle = \langle X_l^2\rangle \, \delta_{lk} O\left(\frac{1}{N}\right)\right)$ in the q-space except $q=0$:

$$\chi^T_{q\neq 0} = \beta\langle X_l^2\rangle. \tag{2.10}$$

The SPT-temperature T_c is reached if $\chi^T_{q=0}$ diverges:

$$f_0\langle X_l^2\rangle = T \quad (f_0\langle X_l^2\rangle < T \text{ for } T > T_c). \tag{2.11}$$

The mean square displacements can be calculated numerically:

$$\langle X_l^2\rangle = \frac{\int e^{-\beta V(X)} X^2 \, dX}{\int e^{-\beta V(X)} \, dX}, \quad V(X) = -\tfrac{1}{2}(1-f_0)X^2 + \tfrac{1}{4}X^4. \tag{2.12}$$

Equations (2.8), (2.10), (2.11) and (2.12) determine the whole thermodynamics of the system above T_c. However no difference between the possible channels of χ^T-divergence at T_c can be done on this level.

3. Long time correlations

If long time correlations

$$L_{lk} = \lim_{t\to\infty} \langle x_l(t) \cdot x_k\rangle \equiv \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^\tau dt \langle x_l(t) \cdot x_k\rangle \tag{3.1}$$

appear we can introduce a new isolated (or Kubo-) susceptibility

$$\chi^K_q = \chi^T_q - \beta L_q = \beta \cdot \langle X^2\rangle^{is}_q \quad \text{with} \quad \langle X^2\rangle^{is}_q = \langle X^2\rangle_q - L_q \tag{3.2}$$

χ^K_q is the susceptibility of a system when switching on the perturbation field adiabatically slow ($\sim e^{\delta t}$, $\delta \to +0$, $t<0$) [12]. In this case the identical linear response approach leads to

$$X^K_{q=0} = \frac{1}{\dfrac{T}{\langle X_l^2\rangle^{is}} - f_0}. \tag{3.3}$$

Thus at T_c $\chi^K_{q=0}$ doesn't diverge and the divergency of the static susceptibility (2.8) is realized through a divergency of $L_{q=0}$ (cf. (3.2)):

$$\chi^T_{q=0}(T \to T_c) = \beta L_{q=0}(T \to T_c). \tag{3.4}$$

With (2.8), (2.10), (3.2), (3.3) it follows

$$L_{q=0} = \frac{1}{(1 - f_0 X^T_{ll})(1 - f_0 \chi^T_{ll} + \beta f_0 L_{ll})}. \tag{3.5}$$

Equation (3.5) shows that if L_{ll} doesn't vanish it follows $L_{q=0} \neq 0$ and the divergency of the static susceptibility goes through a divergency of the long time correlations for $q=0$ and not through the isolated susceptibility. The squared averaged phonon frequency

$$\Omega^2_{q=0} = 1/\chi^K_{q=0} \tag{3.6}$$

doesn't soften completely as it was calculated by Onodera [8]. It should be noted here that the denominator of the right side in (3.5) suggests a second instability when $1 - f_0 \chi^T_{ll} + \beta f_0 L_{ll} = 0$ is reached. However this condition is never fullfilled since at the higher temperature

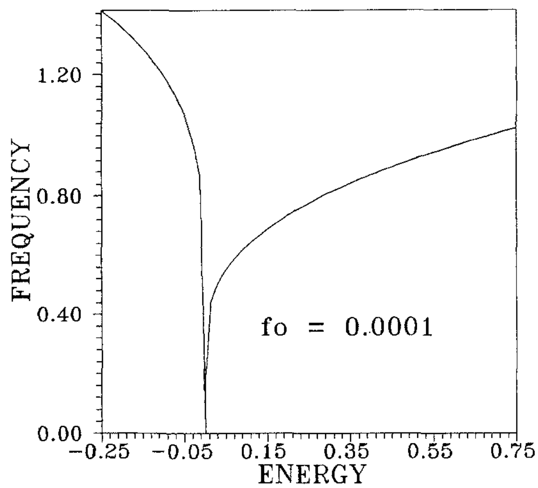

Fig. 1. Frequency of the oscillation of a particle in the potential (2.12) versus energy

T_c the condition $1-f_0\,\chi_{ll}^T=0$ is reached and new expressions for L_q have to be evaluated for $\langle X_l\rangle \neq 0$.

From (3.5) it is seen that calculating the local LTC and the full mean square displacements $\langle X_l^2\rangle$ one can describe all features of model (2.6). The calculation of L_{ll} can be done using (3.1):

$$L_{ll}=\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau \mathrm{d}t\langle x(t,P,X)\cdot X\rangle. \tag{3.7}$$

Since the dynamics of the particle in the potential $V(X)$ (2.12) is always restricted to a finite volume, its motion is periodically with some fundamental frequency ω depending on the energy $E(P,X)$:

$$\omega(E)=\sqrt{2}\,\pi\left(\int_{X_{\min}}^{X_{\max}}\frac{\mathrm{d}X}{\sqrt{E-V(X)}}\right), \tag{3.8}$$

where $X_{\min}$ and $X_{\max}$ are the points of return for a given energy (for negative energies in one of the minima of $V(X)$). the resulting $\omega(E)$-dependence was calculated numerically (Fig. 1) in analogy to Onodera [8]. Now one can carry out the limes in (3.7):

$$L_{ll}=\langle\bar{x}(t,X,P)\cdot X\rangle \tag{3.9}$$

where $\bar{x}(t,X,P)$ is the time-averaged position of the particle with energy $E(P,X)$ over one period. Practically $\bar{x}$ depends only on E and the sign of the initial position X if the energy is negative, while for positive energies the time-averaged position is equal to zero. Substituting the P-integration in the thermodynamical average in (3.9) by an energy integral one gets for $f_0<1$:

$$L_{ll}=\frac{2}{Z}\int_{-\frac{(1-f_0)^2}{4}}^{0}\mathrm{d}E\cdot e^{-\beta E}\;\frac{\left[\int_{X_{\min}}^{X_{\max}}\mathrm{d}X\frac{X}{\sqrt{E-V(X)}}\right]^2}{\int_{X_{\min}}^{X_{\max}}\frac{\mathrm{d}X}{\sqrt{E-V(X)}}},\quad f_0<1. \tag{3.10}$$

Here the fact was used that positive energies are not contributing to L_{ll}. For $f_0>1$ no long time correlations appear:

$$\begin{aligned}&L_{ll}\neq 0,\quad f_0<1\\&L_{ll}=0,\quad f_0>1\end{aligned} \tag{3.11}$$

It is interesting to notice that in the corresponding quantum statistical formulation from the existence of LTC it follows that some local conservation laws must exist [13]. In our case these conservation laws seem to be connected with the phase separation of model (2.6). Since the model (2.6) is integrable and therefore nonergodic it is evident that LTC appear in the case of phase separation ($A>0$).

4. The central peak

As it was shown by Aksenov et al. [3] the appearance of LTC in the displacement-displacement correlation function leads to a $\delta(w)$-peak in the van Hove-scattering function $I_q(w)$ at zero frequencies:

$$\begin{aligned}I_q(w)&=\frac{w}{\pi}\frac{1}{e^{-\beta w}-1}\cdot Im\left[\int \mathrm{d}t\cdot e^{i(w+i\delta)t}\cdot\langle x_l(t)\,x_k\rangle_q\right]_{\delta\to+0}\\&=L_q\cdot\delta(w)+I_{q,\mathrm{reg}}(w)\end{aligned} \tag{4.1}$$

where $I_{q,\mathrm{reg}}$ is the regular part of I_q. Thus nonvanishing LTC produce a central peak and they are one possible reason for the occurence of this phenomenon in real systems [1, 9, 10]. It is interesting to notice that we get a central peak without any defects in our system, although defects are often used to explain this phenomenon [1, 2]. From the projection operator technique applied to the Φ^4-system in [3] it follows exactly

$$L_q=T\frac{\chi_q^T\cdot S_q}{1/\chi_q^T+S_q} \tag{4.2}$$

where S_q is the pole of the Laplace transformed self energy of the relaxation function at $z=0$ (see [3]). This quantity S_q is usually calculated from experimental data [9, 10]. Thus S_q

$$S_q=\frac{T}{\langle X^2\rangle_q}\cdot\frac{L_q}{\langle X^2\rangle_q-L_q} \tag{4.3}$$

is a value of direct proof with experimental findings. Of course in real systems the existence of additional degrees of freedom leads to a transformation of the $\delta(w)$-function in (4.1) into an usual peak at zero frequencies. However the intensity of this peak and its dispersion and T-dependence seem to be determined mainly by $L_q(T)$.

If quantum effects are allowed the tunneling process destroys the LTC and transforms the $\delta(w)$-peak into two splitted peaks at $w=\pm w_{\mathrm{tun}}\neq 0$ [8]. However if the measuring time is shorter than the mean tunneling time $2\pi/w_{\mathrm{tun}}$ a pseudononergodicity criterion defined by Kay [14] leads to the same equations written above in the classical case (i.e. we restrict our time average on time intervals smaller than the tunneling time).

5. Results and discussion

In a first step we have calculated the full mean square displacements (2.12) as a function of temperature for different interaction strength f_0 (Fig. 2). For high temperatures we get the usual increasing of $\langle X_l^2 \rangle$ with T thus producing T-dependent phonon frequencies. In analogy to [8] the differencies between different interaction strengths vanish at high enough temperatures since the X^4-term is dominating. At low temperatures and for small f_0 we find a minimum in $\langle X^2 \rangle (T)$ at some temperature of the order of the energy barrier ΔE in $V(X)$: $\Delta E = 1/4$. This minimum indicates that static ising-like fluctuations begin to dominate with decreasing temperature. A direct comparison with the results of Onodera [8] is not easy since he introduced another dimensionless Hamiltonian than in our case (2.3).

Since our calculations are restricted to the high-symmetry phase ($T > T_c$, $\langle X_l \rangle = 0$) where no mean field appear, we have to calculate the phase diagram $T_c(f_0)$ using (2.11) and (2.12). For weak interaction $f_0 < 0.2$ $T_c(f_0)$ can be asymptotically described by $T_c = f_0$, while for strong interaction $f_0 > 1$ we get $T_c \simeq f_0/3$ (see Fig. 3).

Now one can calculate the local LTC from (3.10) for different interaction strength. The results are shown in Fig. 4. First we want to point out that LTC exist up to arbitrary high temperatures. Thus no abrupt transition into a state with $L_{ll} = 0$ was found in contrary to the results of Aksenov et al. [3] and Flach [15, 16] where a mode-coupling approximation for the relaxation functions within the projection technique of Mori [17] and Tserkovnikov [18] was used. Moreover no plateau up to some temperature (which then would be connected with the barrier height ΔE) in the $L(T)$-dependence was found even for weak interaction. In the case of the existence of such a plateau one could expect the abrupt transition within the mode-coupling approximation being the end of the corresponding plateau. However no

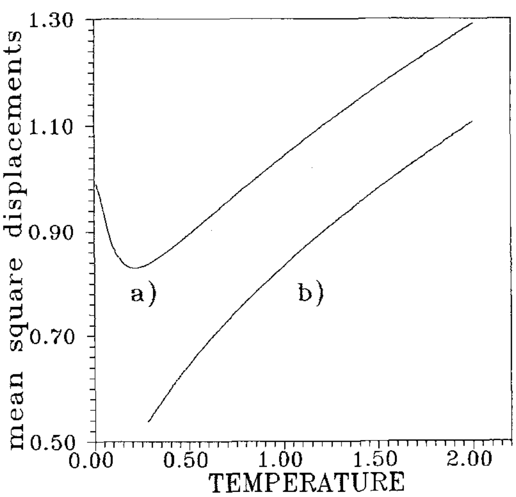

Fig. 2. Mean square displacements versus temperature a) $f_0 = 0.0001$ b) $f_0 = 0.5$ ($T > T_c$)

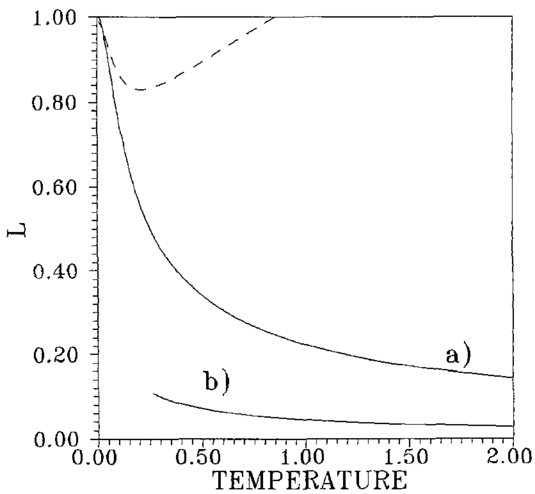

Fig. 4. Long time correlations versus temperature a) $f_0 = 0.0001$ b) $f_0 = 0.5$. The dashed lines is $\langle X^2 \rangle$ in the case a). For $T \to 0 \langle X^2 \rangle \approx L$

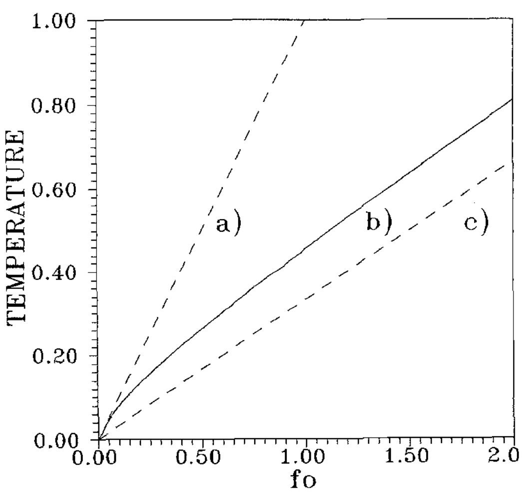

Fig. 3. Phase diagram of model (4): a) $T = f_0$ b) $T_c(f_0)$ c) $T = f_0/3$

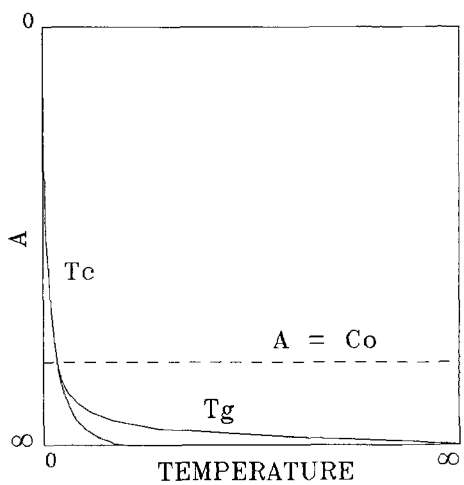

Fig. 5. Qualitative phase diagram of model (2.6) in the special case $B = 1 + A$ comparable with results of [20, 21, 23]. T_G marks the line $L_{q=0} = 0.5 \langle X^2 \rangle_{q=0}$

plateau is found due to the $\omega(E)$-dependence in our case. If the potential $V(X)$ in (2.12) would be replaced by an overlap of two X^2-potentials with minima at $\pm X_0$ then for $E<0$ the $\omega(E)$-spectrum is simply a constant and a plateau in the $L(T)$-behaviour appear up to $T \approx \Delta E (L=1-e^{-\Delta E/T})$. However in this special case it is difficult to make a mode coupling approximation so far as we need nonlinear forces to get nonvanishing LTC (see [3]) within this approach but except the point $X=0$ where the force is discontinuous only harmonic forces appear in the case of piecewise harmonic potentials. In a coming paper [19] we will discuss the reasons of the disagreement between mode coupling approximations and our exact results. At this point we want only state that the mode coupling approximation (decoupling of correlation functions $\langle X^3(t)\, X^3\rangle$ into powers of $\langle X(t)\, X\rangle$) works quite good for small decoupling times t [19] and fails for infinite decoupling times $t \to \infty$.

It is interesting to point out that in the case of short range interaction (next neighbours) a renormalization group theory analysis yields the existence of ising-like fluctuations in the fluctuation spectrum up to arbitrary high temperatures [20, 21]. Since in this case a qualitative phase diagram was calculated, we show such a diagram defining the crossover displacive↔order-disorder at a temperature T_G using the condition $L_{q=0} = 0.5\langle X^2\rangle_{q=0}$ in analogy to [20] (Fig. 5). The main difference between the short-range interaction and infinite range interaction is the vanishing of ising-like fluctuations in the latter case for for $f_0>1$ while in the first case such fluctuations exist for arbitrary interaction strength at arbitrary high temperatures (with decreasing weight for $T\to\infty$). It is still an open question whether there exist long-time correlations in model (2.3) for finite range interaction or not. The appearance of LTC is connected with the appearance of so-called precursor cluster of the low-symmetry phase above T_c [3, 9]. Since such cluster were found in finite Φ^4-systems with next neighbour interaction using molecular dynamical calculations [22] it seems possible to get long time correlations in such a system after carrying out the thermodynamical limes. However the correlations can decay at too long times, i.e. a second characteristic time scale is possible as it was found by studying the soliton-like kinks in extended one-dimensional Φ^4-systems [23]. In our case of infinite range interaction the existence of LTC is clearly depending on whether there is a phase separation at some energies of the system ($f_0<1$) or not ($f_0>1$).

Now let us discuss the dispersion of the LTC (Fig. 6). It is in qualitative agreement with neutron scattering results [9]. For high enough temperatures there are practically no differencies between $L_{q=0}$ and $L_{q\neq 0}$ while for $T\to T_c$ the difference between both values diverge.

Finally we calculated the parameter $S_{ll}(T)$ from eq. (4.3) (see Fig. 7a). For comparison we show the experimentally determined corresponding curve for $RbCaF_3$ [9] in Fig. 7b. The qualitative T-dependence looks similar for both cases. A parameter fit was not possible, since the microscopical model for such a perovskite system needs more parameters than in (2.3) [15]. In the case of $SrTiO_3$ [9] the situation is changed – the measured

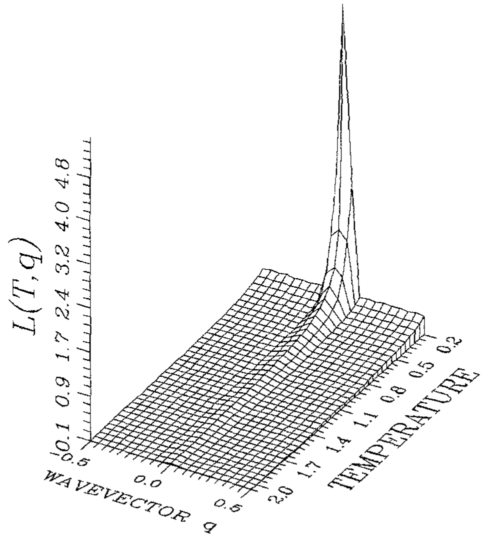

Fig. 6. T- and q-dependence of the long-time correlation function for $f_0=0.2$ (a finite q-step ($\Delta q=0.1$) during plotting provides a finite width of the $L(q)$-peak, however $Lq\neq 0 = L_{ii}$ is assumed)

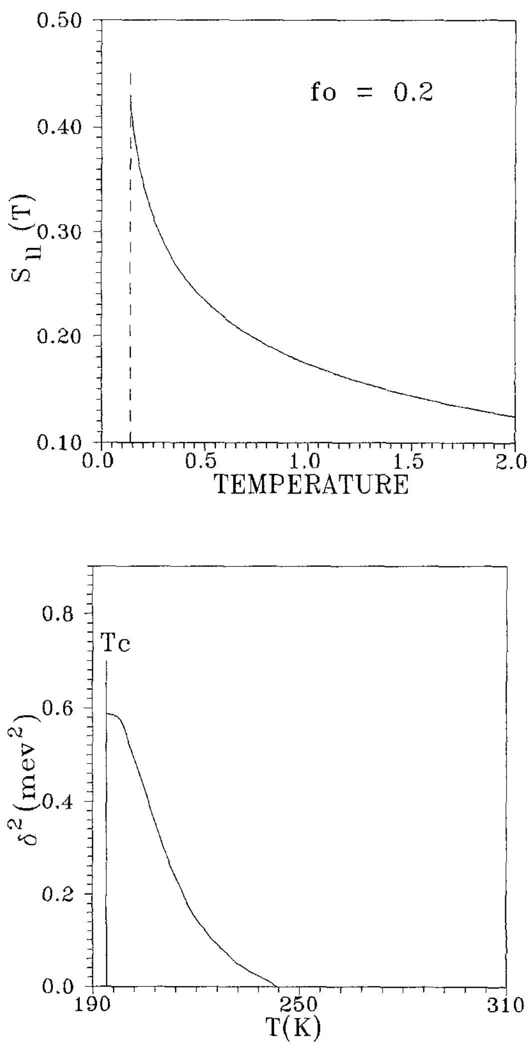

Fig. 7. a The Laplace transformed self energy of the relaxation function at $z=0$ versus temperature.
b The measured self energy for $RbCaF_3$ (from [9])

S_q tends to zero as T tends to T_c. From (4.3) it follows that then LTC must also decrease with decreasing temperature. May be quantum fluctuations ($T_c = 105$ K) or strong anisotropies in the dispersion for $SrTiO_3$ change the behaviour of $L(T)$. Defects seem not to be the source of this disagreement since different crystals with different defects and their concentration yield the same $S_q(T)$ dependence for $T \rightarrow T_c$ [9].

6. Summary

We have demonstrated that for the scalar ϕ^4-lattice model with infinite range interaction long time correlations appear above the phase transition if the interaction is weak enough and calculated their temperature dependence. Then we can easily explain the existence of a central peak in the scattering function of a crystal with a structural phase transition applying our model results. Qualitative agreement with experiments is found. We want to point out that a defect free system was used and thus the LTC appear only due to the phase separation of the effective one-particle potential at low energies. The results of a corresponding mode coupling approximation indicate difficulties of this approach in our case.

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