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NON-ERGODIC BEHAVIOUR IN A STRUCTURAL PHASE TRANSITION MODEL

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INTRODUCTION

In recent years the methods of nonlinear physics have promoted an essential development of the classical theory of soft mode in structural phase transitions [1]. The study of low-dimensional systems has shown that in the region of phase transition at $T > T_c$ there appear dynamical clusters of short-range order preceding an ordered state. Critical behaviour of the system is determined by the dynamics of virtual domain walls whose diffusion results in a central peak in the scattering function; also a qualitative change occurs in the behaviour of the soft mode [2].

No unique answer is at present to the question whether there exist stable formations of the type of clusters of short-range order in the real three-dimensional space. The corresponding nonlinear equations at $d = 3$ may be solved only numerically, with considerable difficulties. For this reason, it is rather difficult to interpret the experimental data many of which point to the existence of clusters in the real systems [3].

Therefore, it would be very useful to establish a general criterion for the appearance of clusters of short-range order. As a criterion of that sort one can take the non-ergodic behaviour of the system for which the isolated susceptibility can possess the zero-frequency anomaly [4]. In this case the isolated susceptibility does not coincide with the isothermal one measured experimentally. Such a state of the system is analogous to the state in low-symmetric phase where the order parameter is a non-ergodic quantity [5], with the only difference that this state is due to the clusters with finite lifetime.

This idea, to our knowledge, was first put forward by Feder [6] and developed by many physicists (see the discussion in the review article [1] sec.3.3). However, it has not been completed since the most consistent consideration of the dynamical behaviour in the region of phase transition within the methods of renormalization group deals with a narrow vicinity of the critical point [1].

In this paper, we apply a recently developed technique of projection operators in the method of double-time Green function [7] to study the conditions of appearance of the non-ergodic behaviour in a particular model of the structural phase transition in dependence on the model parameters and anisotropy of the spectrum of fluctuations of order parameter. The method of ref. [7] allows, in principle, a consistent calculation of the non-ergodicity constant in a wide temperature range; and thus, it becomes possible to establish a general criterion for the non-ergodic behaviour of the system, in particular, clusters of short-range order in the region of phase transition.

As the non-ergodicity is an intrinsic property of phases of the type of spin glass [8,9], the cluster state of the system may be considered as a glass-like phase, in the present case, as a structural-glass phase. Until now the notion "structural glass" was used in studying crystals with defects and solid solutions in which there are competing interactions occurring together with structural disorder [10]. According to our analysis, the state of structural glass may also occur in the region of phase transition in ideal (defectless) systems due to strongly developed nonlinear fluctuations.

1. MODEL AND NONERGODIC CONSTANT

We consider a model of coupled anharmonic oscillators usually used to study structural phase transitions both of the displacive and order-disorder types (see, e.g., [1]):

$$H = \sum_{\ell} (\frac{1}{2} \pi_{\ell}^2 - \frac{1}{2} A Q_{\ell}^2 + \frac{1}{4} B Q_{\ell}^4) + \frac{1}{4} \sum_{\ell,k} C_{\ell k} (Q_{\ell} - Q_k)^2, \qquad (1)$$

where π_{ℓ} and Q_{ℓ} are canonically conjugated local normal momenta and coordinates that obey commutation relations: $[\pi_{\ell}, Q_k] = -i\hbar\delta_{\ell k}$. The single-site potential in (1) describes an anharmonic oscillator with the negative squared harmonic frequency, $-\nu_0^2 = -A < 0$, and the quartic anharmonic interaction of strength $B > 0$. The harmonic force constants $C_{\ell k}$ couple these oscillators on a d-dimensional lattice, $\ell = 1 \dots N$.

To study relaxation processes in the model we introduce the isothermal relaxation function [11]:

$$\Phi_{\ell k}(t) = (u_{\ell}(t), u_k) = \int_0^{\beta} d\tau < u_{\ell}(t - i\tau) u_k > \qquad (2)$$

that defines the thermodynamical average $<\dots>$ of the time-dependent displacement operators $u_{\ell}(t) = Q_{\ell}(t) - <Q_{\ell}>$ at temperature $T = 1/\beta$. The initial value of (2) determines the static isothermal susceptibility:

$$\chi^T_{\ell k} = \Phi_{\ell k}(t=0) = (u_{\ell}, u_k). \qquad (3)$$

If a system is nonergodic, some correlations in it do not decay with time t that results in nonzero values of the corresponding correlation functions in the limit $t \to \infty$. We define the

nonergodic constant for the model (1) by

$$L_{\ell k} = \lim_{t \to \infty} < u_{\ell}(t) u_k > = \lim_{\epsilon \to 0} \epsilon \int_t^{\infty} dt' e^{-\epsilon t'} < u_{\ell}(t') u_k >. \qquad (4)$$

As was shown by Kubo [12], this constant is equal to the difference of the static isothermal (3) and isolated (or Kubo) $\chi^K_{\ell k}$ susceptibilities and can be calculated as:

$$\beta L_{\ell k} = \lim_{z \to i0} z \Phi_{\ell k}(z) = \chi^T_{\ell k} - \chi^K_{\ell k}, \qquad (5)$$

where the Laplace transform is given by

$$\Phi_{\ell k}(z) = \frac{1}{i} \int_0^{\infty} dt e^{izt} \Phi_{\ell k}(t) = ((u_{\ell} | u_k))_z, \quad \mathrm{Im}\, z > 0. \qquad (6)$$

By applying the projection-operator technique proposed by Tserkovnikov [7] that is equivalent to the continued fraction expansion of Mori, one obtains for the relaxation function (6) in the q-representation:

$$\Phi_q(z) = \chi^T_q \frac{1}{z - \dfrac{1/\chi^T_q}{z - M_q(z)}}, \qquad (7)$$

where

$$\Phi_{\ell k}(z) = \frac{1}{N} \sum_q \Phi_q(z) e^{iq(\ell - k)}. \qquad (8)$$

The relaxation kernel $M_q(z)$, or the self-energy operator, is given by the irreducible part of second order (see [7])

$$M_{\ell k}(z) = B^2 ((u^3_{\ell} | u^3_k))_{(2)}. \qquad (9)$$

The static limit for the relaxation function (7) yields the nonergodic constant (5) in the form

$$\beta L_q = \lim_{z \to i0} [z \Phi_q(z)] = \lim \chi^T_q \frac{z M_q(z)}{1/\chi^T_q + z M_q(z)} = \chi^T_q - (1/\chi^T_q + s_q)^{-1}, \qquad (10)$$

where

$$s_q = \lim_{z \to i0} z M_q(z). \qquad (11)$$

If we assume the system (1) to undergo a structural phase transition of the ferrodistortive type, at some temperature T_c, then its susceptibility at $\tau = T/T_c - 1 \to 0$ and $q \to 0$ can be written in the form:

$$\chi_q^T = (a|\tau|^\gamma + C_0 - C_q)^{-1}, \tag{12}$$

where $C_q = \sum_\ell C_{0\ell} e^{iq\ell}$, $C_0 = C_{q=0}$. In this case from eqs.(5) and (10) the following expression for the Kubo susceptibility can be obtained:

$$\chi_q^K = (a|\tau|^\gamma + s_q + C_0 - C_q)^{-1}. \tag{13}$$

It becomes divergent at some temperature T_0 lower than T_c:

$$T_0 = T_c[1 - (s_{q=0}/a)^{1/\gamma}] \tag{14}$$

provided that $s_{q=0}$ is finite at $T \to T_c$.

To estimate the relaxation kernel (9), we employ the mode-mode approximation [8] in the form:

$$M_{\ell k}(z) \approx \frac{B^2}{i} \int_0^\infty dt\, e^{izt} \int_0^\beta d\tau\, 6 < u_\ell(t - i\tau) u_k^3 >, \tag{15}$$

where the correlation function is given by:

$$< u_\ell(t) u_k > = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega\, \omega}{e^{\beta\omega} - 1} e^{-i\omega t} \operatorname{Im}\Phi_{\ell k}(\omega). \tag{16}$$

The singular part of (15) is defined by the non-ergodic contribution (4) of the correlation function (16) and after integration the q-representation of eq.(15) can be written as

$$M_q(z) = \frac{1}{z} 6\beta B^2 \frac{1}{N^2} \sum_{q_1, q_2} L_{q_1} L_{q_2} L_{q_1+q_2-q} + M_q^{reg}(z). \tag{17}$$

Now after the calculation of the static limit in eq.(11) with the function (17) one obtains a closed system of equations (10), (12), (17) for the non-ergodic constant L_q.

2. NON-ERGODIC BEHAVIOUR OF THE MODEL

For a qualitative discussion we may further simplify the relaxation kernel (15) by adopting a single-site approximation: $M_{\ell k}(z) \sim \delta_{\ell k} M_{kk}(z)$ that results in the q-independent $s = 6\beta B^2 L_{kk}^3$

in eq. (11) and the following self-consistent equation for $L = L_{kk}$:

$$\beta L = \frac{\beta}{N} \sum_q L_q = \frac{1}{N} \sum_q (\chi_q^T - \frac{1}{1/\chi_q^T + 6\beta B^2 L^3}). \tag{18}$$

To solve eq.(18) for L one should also calculate self-consistently the static susceptibility χ_q^T in eq. (3). In the present investigation, however, we have adopted a model approach by introducing in eq. (18) the susceptibility in the form of eq.(12). In this way, one obtains a non-linear equation for L(T).

For integration over q in eq.(18) we will describe the spectrum of order parameter fluctuations in the following model form:

$$C_0 - C_q = C(\kappa^2 q_\perp^2 + q_z^2) \tag{19}$$

and choose in eq.(12) $\gamma = 1$, $a = A$ for $\tau > 0$. Approximating the Brillouin zone by a cylinder (diameter $2q_0$, height $2q_0$) the q-integrations are performed according to

$$\frac{1}{N} \sum_q F[C_0 - C_q] = 2 \int_0^1 d\rho\, \rho \int_0^1 dz\, F[A f_0 (\kappa^2\rho^2 + z^2)], \tag{20}$$

where F[x] is an arbitrary function and $f_0 = q_0^2 C/A$. By the use of the dimensionless variables

$$\ell = BL/A, \quad \Theta = BT/A^2, \quad \Delta_0^2 = |\tau|/f_0, \quad \Delta_1^2 = (|\tau| + 6\ell^3/\Theta)/f_0 \tag{21}$$

we obtain from (18) the following transcendental equation for ℓ

$$\ell = (2\Theta/f_0\kappa^2)[g(\Delta_0) - g(\Delta_1)] \tag{22}$$

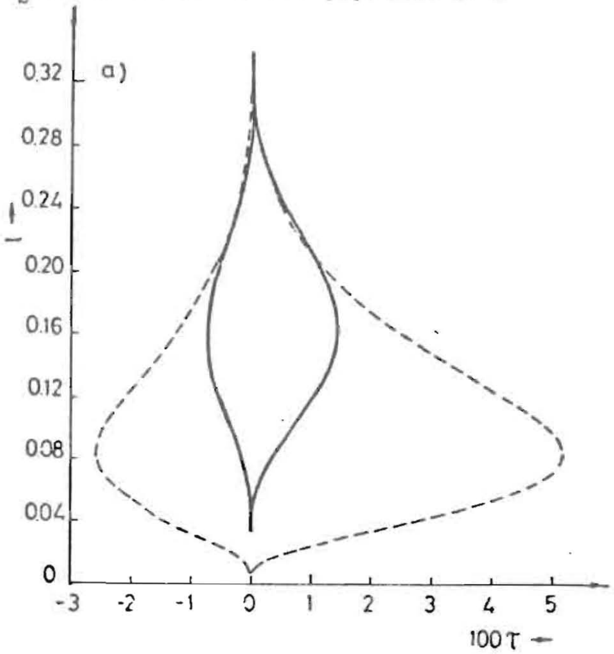
with

$$g(\Delta) = \frac{1}{2}\ln(1 + \kappa^2/(1+\Delta^2)) + (\Delta^2 + \kappa^2)^{1/2} \arctan(\Delta^2 + \kappa^2)^{-1/2} - \Delta\arctan(1/\Delta). \tag{23}$$

Investigation of eq.(22) shows that besides the trivial solution $\ell = 0$ in the vicinity of T_c there are two nonzero solutions ℓ_1, ℓ_2 in some temperature interval $\Theta_c \le \Theta \le \Theta_g$ and for the coupling parameter $f_0 < f_g$ at a fixed anisotropy parameter κ.

For a numerical analysis of (22) the critical temperature $\Theta_c = BT_c/A^2$ has been related to the parameters of our model using the self-consistent phonon approximation [13]. Correspondingly, the ferrodistortive phase transition takes place at $<u^2>_c = A/3B$ with $<u^2>_c = (T_c/N)\sum_q \chi_q^T$, which gives $\Theta_c = \kappa^2 f_0/(3\ln(1+\kappa^2) + 6\kappa\arctan(1/\kappa))$.

The solutions of (22) have been plotted in Fig.1 for special parameters f_0 and κ. At $r = r_g(f_0, \kappa)$ they appear discontinuously (first-order transition to a non-ergodic state) with $\ell_1 = \ell_2 = \ell_g$ and for $r < r_g$ we have $\ell_1 < \ell_g < \ell_2$. From the point of view of thermodynamic stability, in correspondence with ordinary phase transitions, solution $\ell_2(T)$ seems to be the physical one.



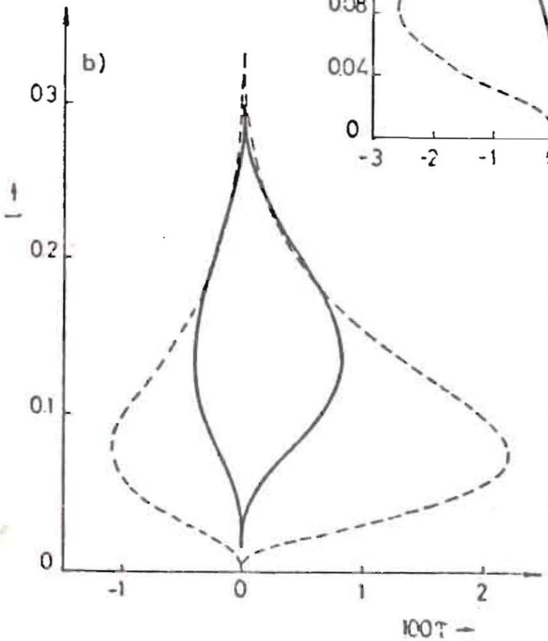


Fig. 1. Dependence of the non-ergodicity constant ℓ *on the reduced temperature* $r = (T - T_c)/T_c$; *a) the isotropic case* ($\kappa = 1$), $f_0 = 0.1$ *(dotted line)*, $f_0 = 0.5$ *(solid curve), b) the anisotropic case* ($\kappa = 0.1$), $f_0 = 2$ *and* $f_0 = 10$ *dotted and solid curves, respectively.*

The case $r < 0$ has been treated as $r > 0$ but with $a = 2A$ in the susceptibility (12). Correspondingly, r in eqs.(21) has been replaced by $2r$. The results are, of course, analogous to the case $r > 0$.

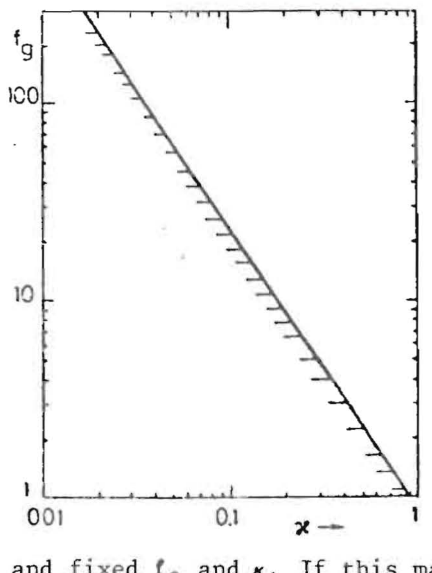


Fig. 2. Dependence of the critical value of the coupling constant f_g *on the anisotropy parameter* κ. *For* $f_0 < f_g$ *the system is specified by the non-ergodic behaviour.*

Let us emphasize that nonzero solutions exist only for certain values of $f_0 : f_0 < f_g$, and as one can see from Fig.2, the value of f_g increases as the anisotropy of the system increases (or as the parameter κ decreases). The line in Fig.2 has been obtained by calculating the maximum of the rhs of (22) divided by ℓ as a function of ℓ for $r = 0$ and fixed f_0 and κ. If this maximum is lower than one, there are no nonzero solutions. It is interesting to point out that the result on non-ergodic behaviour of the model can even be obtained if one employs a more crude approximation in (18) by performing the q-integration in the following manner

$$\bar{\chi}^T = \frac{1}{N}\sum_q \chi_q^T = \frac{1}{A(|r| + f_0)}. \tag{24}$$

This mean-field type approximation when order parameter fluctuations are neglected results in a simple equation for ℓ

$$\ell\left[\ell^3 - \frac{\Theta}{|r| + f_0}\ell^2 + \frac{1}{6}\Theta(|r| + f_0)\right] = 0 \tag{25}$$

that can be solved analytically. Its nonzero solutions appear again at a temperature $\Theta = \Theta_g$ (or $r = r_g$) where $\ell_1(\Theta_g) = \ell_2(\Theta_g) = \ell_g = (r_g + f_0)/\sqrt{2}$ and r_g is given by

$$r_g = (1-a) f_0 \left[(1 + (2a/f_0 - 1)/(1-a))^{1/2} - 1 \right], \quad a = \sqrt{2}/9. \tag{26}$$

This expression has been derived using the MFA $\Theta_c = f_0/3$ obtained from the estimation $\langle u^2 \rangle_c = T_c \bar{\chi}^T = A/3B$. From (26) it follows that also in this simple approximation solutions exist only for $f_0 < f_g = 2a \approx 0.31$ although this result is considerably smaller than the corresponding value $f_g \approx 0.85$ calculated from (22). The critical value of ℓ is $\ell = \ell_g = 2/9$. Equation (26) allows us to obtain also the estimation for r_g at $f_0 \approx f_g$:

$$r_g = \frac{1}{2}(f_g - f_0). \tag{27}$$

So, the non-ergodic behaviour of the model is defined by the model character and its parameters, i.e., it is a qualitative property of the model. Taking account of fluctuations may lead only to a quantitative change of critical values though highly considerable.

Let us note that in paper [14] it has been shown in the mean-field approximation that the system (1) becomes Ising-like at the parameter f_0 close to f_g (at $f_0 \approx 0.25$).

DISCUSSIONS

The main result of the present investigation of the well-known model (1) for structural phase transition is the occurrence of non-ergodic behaviour of the system of anharmonic oscillators in the vicinity of the temperature of phase transition T_c. This non-ergodic behaviour with the constant $L_{\ell k} \neq 0$ (4) appears as a consequence of a pole at $z = 0$ in the relaxation kernel (11). The non-ergodic behaviour physically results in the difference of static isothermal (12) and isolated (13) susceptibilities (see eqs. (5), (10)) that diverge in the case at different temperatures given by eq. (14). There is also a static central peak in the van Hove scattering function

$$S(q,\omega) = -\frac{1}{1-e^{-\beta\omega}}\frac{\omega}{\pi}\,\mathrm{Im}\,\Phi_q(\omega + i\epsilon) = L_q\,\delta(\omega) + S_{reg}(q,\omega), \tag{28}$$

where the last term is the regular part of the function.

The non-ergodic behaviour of the system is possible when its susceptibility χ_q^T is sufficiently high: as it follows from the general eq. (10) or its approximated version (18), a nonzero solution, $L \neq 0$, appears when $(\chi_q^T)^{-1} \ll S_q \approx 6\beta B^2 L^3$. In this limit $L = (1/N)\Sigma_q \chi_q^T$ which shows that the main contribution for the fluctuations in the system comes from the non-ergodic (static) fluctuations and not from the dynamical ones described by the Kubo susceptibility (13): $\chi_q^K = ((\chi_q^T)^{-1} + s_q)^{-1} \ll \chi_q^T$.

The estimations in §2 reveal that non-ergodic behaviour appears in some temperature range $T_g^- \le T \le T_g^+$ where the values $T_g^- \le T_c \le T_g^+$ depend mainly on the dimensionless coupling constant $f_0 = \Sigma_j C_{ij}/A$: there is only a zero solution, $L = 0$, for $f_0 > f_g$ and $T_g^- = T_g^+ = T_c$ for $f_0 = f_g$. The absolute value f_g critically depends on the approximations for the fluctuation spectrum of the model: for isotropic spectrum ($\kappa = 1$ in eq. (19)) $f_g \approx 0.85$, but at the same time at $\kappa = 0.1$, $f_g \approx 20$. This result completed with comments made in the Introduction suggests that non-ergodic behaviour of the model originates from the clusters of short-range order. Therefore, the non-ergodic behaviour of the model specified by the constant of non-ergodicity L may serve as a criterion of the clusters of short-range order or crossover from the displacive regime to the order-disorder regime. This criterion is an alternative criterion of transition of the system into a cluster state proposed in refs. [15-17].

As to the latter comment, we note the following: it is usually assumed [1] that the clusters of short-range order appear owing to critical fluctuations. In our opinion, it is not so. This is, in particular, testified by our result in the mean-field approximation. The appearance of clusters leading the system to a non-ergodic state is caused by nonlinearity of the system that can be strong and beyond the critical region.

From the standpoint of non-ergodic behaviour of the system its state in the presence of clusters of short-range order may be identified with the phase of structural glass, and the constant of non-ergodicity may be treated as a sign of that phase. The connection between the dynamical transition from ergodic to non-ergodic behaviour and transition to the phase of spin glass has recently been studied in papers [8,9]. Note also that the investigation of the structural glass phase within the model [1] for solid solutions of components with ferro- and antiferrodistortive interactions [18] and for the system with competing interactions between the nearest and next neighbours [19] shows in fact that the phase of structural glass appears when the mean coupling constant in the system (isotropic) f_0 tends to zero. In the main our consideration was of a qualitative nature. A more rigorous description of non-ergodic behaviour of the model requires a self-consistent calculation of the susceptibility χ_q^T without model representation (12). Results of such a more consistent approach will be published in a subsequent paper.

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