TOWARD ANALYTICAL EXPLANATION OF INCOMPLETE PHONON SOFTENING IN DISPLACIVE STRUCTURAL PHASE TRANSITIONS

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The formation of clusters and their influence on phonons at the displacive structural phase transition in d-dimensional Ising-universality-class model is investigated. It is shown that in the critical point the incomplete phonon softening occurs while a central peak due to relaxation dynamics of clusters appears in the spectral density of excitations.

The principal role of nonlinear effects at structural phase transitions /spt/ has been originally pointed out by Krumhansl and Schrieffer[1]. Thus the exact solution for the one-dimensional/$d=1$/ lattice shows that besides phonons /the softening of which causes the "displacive" phase transition /dpt// there are also the nonlinear/soliton-like/ excitations which independently on /or additionally to/ phonons can lead to the instability of the lattice. This fundamental inference is also consistent with molecular dynamics simulations /for $d=1$ to $d=4$ /[2] as well as with the results of the exact dynamics of few coupled quartic oscillators[3]. In the series of subsequent theoretical works[4-9] it was envisaged that with the onset of criticality a crossover from a "displacive" to an "order-disorder" regime could occur, manifested in the formation of long-lived clusters of precursor order. The existence and dynamics of such clusters give rise to the central peak /c.p.//i.e. the nonclassical critical behaviour/, in that the soft mode being supressed due to the symmetry violation locally /see, e.g.ref. 9/.

While such a physical picture is conceptually quite acceptible, it is still not analitically founded and has also lacked indisputable experimental verification. Nevertheless, by interpreting the recent EPR experiments on monodomain-transforming $SrTiO_3$/through motional-narrowing, using Fe^{3+}-V_o centers/[10], Bruce, Müller and Berlinger[9]/see also ref. 11/ drew attention on the challenging accord between theoretical and experimental estimates of a non-vanishing soft-mode frequency at the phase transition temperature /T_c/, thus prompting further progress in all-inclusive spt-investigations. Apparently, such almost coincidence corroborates the model description[1,9,12] by which the local normal coordinate[13] $s_i(t)$ is decomposed into a slow momentary quasirest position/$r_i(t)$/ and a comparatively fast deviation /$u_i(t)$ around $r_i(t)$/ of the phonon /quasiharmonic/ type. In the frames of such ideas, our preceding works[12,14] were devoted to an analitic spt-description within a single universal model using in addition the variational approach of Bogolyubov. Thus a novel interpolary scheme has been proposed[12] so as attempting to include all the intriguing features of the spt, i.e. statistical order-disorder, tunneling /real or effective / and phonon excitations.

Presently, to describe a possibly order-disorder behaviour of a traditionally displacive spt /apart revealed in an incomplete phonon softening/ the adjusment of our previous model in addition is accomplished by employing both the solitary-waves[1,5,7] and the renormalization-group[15]/rg/ techniques. Note that so far the rg-method has been used in this sense only for order-disorder systems[16].

We consider the widely used model Hamiltonian

$$H = \sum_i \left(\frac{p_i^2}{2m} - \frac{A}{2} s_i^2 + \frac{B}{4} s_i^4 \right) + \sum_{ij} \frac{1}{4} \varphi_{ij} (s_i - s_j)^2 \qquad /1/$$

with the local normal coordinate represented in the form[9,12]

$$s_i = r_i + u_i \; ; \qquad /2/$$

r_i is defined by the quantum-statistical average

$$r_i = \langle s_i \rangle_{ph} = \frac{1}{Z_{ph}} Sp_{\{u_i\}} \left(e^{-H/T} s_i \right) , \qquad /3/$$

u_i being a quasiharmonic deviation around it, the index i labeling N lattice sites.

From the equilibrium condition,

$$\langle i \frac{d}{dt} p_i(t) \rangle_{ph} = \langle [p_i, H] \rangle_{ph} = 0 \qquad /4/$$

/equivalent to minimization of the free energy for a given configuration $\{r_i\}$: $\frac{\partial}{\partial r_i} F(\{r_i\})$; $F(\{r_i\}) = -T \ln Sp_{\{u_i\}} e^{-H/T}$ /., and using the appropriate dimensionless notation

$$\eta_i=\sqrt{B/A}\, r_i \;,\; f_{ij}=(1/A)\varphi_{ij} \;,\; f_q=\sum_j f_{ij}e^{i\vec{q}(\vec{l}_i-\vec{l}_j)} \;; \qquad /5/$$

$$a_i(T)=1-y_i(T)\,,\quad y_i(T)=3(B/A)[\langle u_i^2\rangle_{ph}+(1/3r_i)\langle u_i^3\rangle_{ph}]\,,$$

the quasiequilibrium positions /i.e. the local order parameters η_i / are determined by the nonlinear equation

$$\eta_i[\eta_i^2-a_i(T)]+\sum_j f_{ij}(\eta_i-\eta_j)=0\;. \qquad /6/$$

In the weak-coupling limit, $f_0\ll 1$, a transition of the order-disorder type is possible being described by the effective Ising model[17]/ via pseudospin variables: $\eta_i=\sigma_i\sqrt{a}$, $\sigma_i=\pm 1$/. As the role of fluctuations is not significant in this case[12], $\langle u^2\rangle/(A/B)\sim T/(A^2/B)\ll 1$ at $T\sim T_c\sim f_0(A^2/B)\ll A^2/B$, and therefore $a\approx 1$. Furthermore, when the ground-state-quantum splitting within a local double-well potential plays a predominant role in the dynamics of low temperature spt's, then the kinetic /tunneling/ Ising model is more adequate itself accomodating the additional "intra-well" degrees of freedom[14,18].

In a rather strong coupling limit /$f_0\gg 1$//we are mainly interested for throughout this paper / a slow varying η_i evolves, $|\eta_i-\eta_j|\sim 1/f_0\ll 1$ (eq. 6), so a continuumization, $\eta_i\to\eta(x)$, is possible:

$$\eta(x)[\eta^2(x)-a(x,T)]+\sum_{\alpha\beta}C_{\alpha\beta}\,\partial^2\eta(x)/\partial x_\alpha\partial x_\beta\;, \qquad /7/$$

where the elasticity modulus

$$C_{\alpha\beta}=\sum_j f_{ij}\,\frac{1}{2}\,(x_i^\alpha-x_j^\alpha)(x_i^\beta-x_j^\beta)\;. \qquad /8/$$

In the pseudo one-dimensional case /the only tractable analytically/, the above equation/7/ becomes

$$C\,\frac{d^2\eta(x)}{dx^2}+\eta^3(x)-a(x,T)\eta(x)=0\;, \qquad /9/$$

where in the mean-field approximation /$\langle u^3\rangle=0$/

$$y(x,T)=(B/A)\langle u^2\rangle=(\lambda/2\sqrt{\Delta(x)+f_0})\,cth(\lambda\sqrt{\Delta(x)+f_0})\;; \qquad /10/$$

$$\Delta(x)=3(\eta^2(x)+y(x))-1=3\eta^2(x)-a(x)\,,$$

$\Delta(x)$ being the gap in the phonon spectrum and $\lambda=\hbar\sqrt{A/m}/\frac{A^2}{B}$ is the quantum parameter.

The above system of equations//9/,/10//differs from the corresponding ones in[19] as thermal /in addition to quantum/ effects are taken into account. Further, as $f_0\gg|\Delta(x)|\sim 1$ then $a(x,T)\approx a(T)$ and assuming homogeneous boundary equilibrium positions, $\eta_0 = \eta(x \to \pm\infty)$, one obtains a soliton solution

$$\eta(x) \approx \sqrt{a(T)}\, th(x/\xi\sqrt{2}), \quad \xi = \sqrt{c}/\sqrt{a(T)}. \qquad /11/$$

It is easily seen that phonon fluctuations account /through $a(T)$/ for the decreasing of the soliton amplitude, $\eta = \sqrt{a(T)} < 1$, i.e. increasing of its width $/\sqrt{c/a(T)} > \xi_0 = \sqrt{c}/$. The variation within a domain wall $/x < \xi/$ can be easily /iteratively/ accounted for[19] but the form of the solution/11/ is not substantiately altered. From the demand for the homogeneous solution $\eta(x) = \eta$ /being the order parameter actually/ to vanish identically and eq./6/ one estimates the phase transition temperature /i.e. of the soft-mode condensation $/T_c^o \sim (f_0/3)A^2/B/$ as $y \sim TB/f_0A^2$/.

The unhomogeneous solution/11/ also admits another type of phase transition corresponding to an instability of the whole system with respect to differently oriented clusters $/\eta(x) = \pm\sqrt{a}/$. In that case the dpt can be viewed as a transition of the order-disorder type, i.e. at $T = T_c < T_c^o$: $\eta = \langle\eta(x)\rangle_{cl} = 0$ but $\langle\eta^2(x)\rangle_{cl} \approx a(T_c) \neq 0$, the symbol $\langle\cdots\rangle_{cl}$ denoting the average over all clusters. This picture is dictated by nonlinearity of the model in addition being consistent with the results of the molecular dynamics-methods for d=1 to d=4 dimensions[2,4,8]. To corroborate it more profoundly we consider the behaviour of the probability distribution function of quasiequilibrium positions $P(\eta)$ in the limit $T \to T_c$.

From eq./6/ it is evident that $P(\eta)$ is described by the configuration potential energy of the system. In the rg-analysis it is convenient to use the dimensionless quantities $/r = a/c$, $g = b/4c$ /, so in the continuum version

$$P_{rg}(\eta) = Z^{-1} exp(-H_{rg}(\eta)), \qquad /12/$$

where

$$H_{rg}(\eta) = \beta U_{rg}(\eta) = \frac{1}{2}\int d^d x \{r\eta^2(x) + (\nabla\eta(x))^2 + g\eta^4(x)\}; \beta = T/c \qquad /13/$$

is the standard Landau-Wilson Hamiltonian.

As it is well known, at the critical point $/T_c/$ a stochastic field $\{\eta(x)\}$ /and correspondingly its distribution $P(\eta)$/ is scaling-invariant thus describing a distribution of large-size clusters. It is defined by the fixed point $/r^*, g^*/$ of the rg-transformation (R)

$$R\, P_{r^*g^*}(\eta) = P_{r^*g^*}(\eta), \qquad /14/$$

wherefrom the first order in $\varepsilon \equiv 4-d$ - expansion yields

$$r^* = -\frac{n+2}{n+8}\varepsilon + O(\varepsilon^2) \;;\quad g^* = \frac{8\pi^2}{n+8} + O(\varepsilon^2) \;;\quad n = d\,, \tag{15}$$

/ n - the number of componets of the order parameter /.

For $d \leqslant 3$ $a^* = a(T_c) > 0$ and $P(\eta)$ is non-Gaussian /as distinct from[6], only due to the relaxation dynamics of η_i /.

Keeping in mind that the soft-mode frequency $/\Omega_q/$ is given by the pole of the phonon Green's function $/\omega \to 0/$

$$G_q(\omega) = A\sum_j e^{i\vec{q}(\vec{l}_i - \vec{l}_j)} \langle\langle u_i | u_j \rangle\rangle_\omega = \left\{ (m/A)\omega^2 - [\Delta + f_o - f_q + M_q(\omega)] \right\}^{-1}, \tag{16}$$

$M_q(\omega)$ being the self-energy operator[20], a straightforward inspection of limits $T \to T_c^o$, $q \to 0$ yields

$$\Omega_q^2 \approx \Omega_o^2 + c^2 q^2 \;;\quad \Omega_o^2 = \Delta + M_o(0)\,. \tag{17}$$

While in the homogeneous case, as usual, $\Omega_o(T \to T_c) \to 0$, for $d \lesssim 3$ - on account of nonlinear effects /eqs./6/,/15/ / - one finds $\Omega_o^2(T \to T_c) \to 2\eta^2 = 2a \to -2r^* > 0$. As a consequence, as $T \to T_c$ the dpt turns to be of the order-disorder /Ising/ type governed by the relaxation cluster dynamics, i.e. $\langle \eta_i \rangle_{cl} = 0$, $\langle \eta_i^2 \rangle_{cl} \sim -r^* \neq 0$, while in that a complete phonon softening /i.e. a long-homogeneous order, $\langle \eta_i \rangle = 0$/ fails to come.

To outline the critical cluster dynamics we use the phenomenological equation of Landau-Khalatnikov in the coordinate space /see, e.g. refs. 21, 22 /

$$\partial_\tau \eta - \nabla^2 \eta + r\eta + 4g\eta^3 = 0\,, \tag{18}$$

where Γ is a "kinetic" parameter and $\tau = \Gamma t$. For d=1 this equation has a soliton solution $\eta = f(x - v\tau, \tau)$ in the form / $|v| \gg 1$; $\zeta = x - v\tau$/

$$f^2(\zeta, \tau) = -r/(4g + \exp(-2\zeta\tau/v))\,, \tag{19}$$

which describes a destruction of clusters fluctuately arising around T_c.

The spectrum of η_q- fluctuations /if $g = 0$/ in the "harmonic" approximation is given by[21]

$$I_q(\omega)=\int_{-\infty}^{+\infty}dt\, e^{-i\omega t}\langle\eta_q(0)\eta_{-q}(t)\rangle = \frac{T}{r+q^2}\,\frac{2\tau_q}{1+(\omega\tau_q)^2} = \frac{2T\Gamma}{\tau_q^{-2}+\omega^2}\,, \qquad /20/$$

where

$$\tau_q=[\Gamma(r+q^2)]^{-1}\,; \qquad r\sim a\sim(T-T_c^o)\,, \qquad /21/$$

q being the reduced wave vector.

By settling accounts for nonlinear effects $/g\neq 0/$, using the ansatz[22], the asymptotic spectral response /i.e. when $q\to 0$, $\omega\ll 1$, $T\to T_c$/ exebits a c.p. behaviour, thus reflecting a slow relaxation of "cluster walls":

$$I(q=0,\omega)\sim\frac{T_c\Gamma}{\pi}\,\frac{1}{\omega^{1+(2-\gamma)/\Delta_\omega}}\,. \qquad /22/$$

The combination of the critical $/\gamma/$ and dynamical $/\Delta_\omega/$ indecies is given by the fixed point-parameter $/g^*/$, i.e. by the ε-expansion

$$\frac{2-\gamma}{\Delta_\omega}=1-\frac{(g^*)^2}{64\pi^4}9\ln(4/3)\approx 1-\frac{\varepsilon^2}{2(n+8)}\ln(4/3)\,. \qquad /23/$$

To conclude, our theoretical findings based upon the decomposing picture on "slow" and "fast" dynamical variables /eq./2// show that /in accord with previous results,i.e. with various above mentioned approaches and suitable experiments/ at some/"true"/ critical temperature, $T_c=T_c^o-\Delta T_c$ $/\Delta T_c\sim\varepsilon T_c^o/$, the traditionally dpt systems become structurally unstable against nonlinearly induced precursor clusters /i.e. by their order-disorder, described by Ising-like variables that $\langle\eta_i(T\to T_c)\rangle_{cl}\to 0$ / without a complete phonon softening / $\Omega_q(q\to 0,T\to T_c)\to 2\langle\eta_i^2(T_c)\rangle_{cl}=2a^*\sim\varepsilon$ /, these clusters in addition relaxing in the peculiar /dynamical/ fashion / $I_q(\omega\to 0,q\to 0,T\to T_c)\sim\omega^{-\delta}$, $\delta<2$ /. Finally, it should be gratifying that the present contribution could, in part at least, complete a better understanding of the spt dynamics at all, in that to corroborate possibly all the more appealing idea about the intrinsicly "order-disorder origin" of universality itself.

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