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LETTER TO THE EDITOR

A molecular dynamics study of long-time correlations in a model of structural phase transitions—comparison with a mode-coupling approximation

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Abstract. Predictions of a mode-coupling approximation (MCA) are compared with molecular dynamical simulations of one-dimensional Φ^4-lattice systems with different next-neighbour interaction strengths. In the long-time behaviour we find complete disagreement for weak coupling, whereas some predictions of the MCA are qualitatively verified in the strong-coupling case, indicating different sources for long-time correlations (local phase space separation or soliton-like solutions of non-linear differential equations).

Up to now it has been an open question whether or not the long-time behaviour of the displacement–displacement correlation function S of perovskite crystals causing a narrow central peak (CP) in the van Hove scattering function near structural phase transitions (SPT) [1] can be described using a decoupling procedure in the relaxation kernel of S. This decoupling method (factorization) leads to mode-coupling equations for S, i.e. the relaxation kernel becomes a power of S itself [2]. The approximation will be defined as a mode-coupling approximation (MCA) due to the special character of the resulting equations (see below).

The first step towards answering this question is to define a microscopically motivated model. For many purposes it seems reasonable to choose the Φ^4-lattice model, since most qualitative features of SPT of perovskites are reproduced by it [1] and there exist *ab initio* calculations clearly demonstrating the multiwell character of the lattice potential (of the high-symmetry phase) [3, 4].

Using the MCA, Aksenov *et al* [2] obtained long-time correlations (LTC) $\equiv S(t \rightarrow \infty)$ near the SPT of the Φ^4-model. Moreover they found a transition temperature T_g separating phases with and without LTC ($T_g > T_c$, $T_c \equiv$ SPT temperature). This additional transition is well understood within schematic models of liquid–glass transitions [5]. Götze *et al* ([5] and references therein) solved the slow dynamics of such a schematic model near the singularity point T_g, obtaining scaling laws and well-defined relaxation properties (depending on the model analysed). Hence, it should to be very interesting to investigate the applicability of the mode-coupling theory of liquid–glass transitions to a lattice model describing a SPT.

The result may strongly depend on the interaction range. In [6] the one-component Φ^4-lattice model was studied for infinite-range interactions. In this case

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the LTC appear due to phase space separation of this non-ergodic system for $N \to \infty$ (N integrals of motion, N is the number of unit cells). A comparison of these exact results with a MCA yields good agreement (except for at low temperatures) for zero decoupling times, i.e. for static correlations, and complete disagreement for infinite decoupling times (in which we are interested) [7, 8].

However, in the case of finite-range interaction it is an open question under which conditions and for what reasons LTC may appear. In a great number of molecular dynamics (MD) studies of the Φ^4-model with next-neighbour interaction (NNI) the long-time behaviour of the model was analysed ([9–14] and references therein). However, there has been no systematic study of the applicability of MCA. So our aim was to obtain such information from MD simulations of $d=1$, 2-dimensional Φ^4-systems with NNI.

In this letter we present results on one-dimensional systems. The lack of a SPT in these systems ($T_c = 0$, [15]) does not seem to be important since quasi-one-dimensional systems exhibit a SPT and will also exhibit the properties discussed below.

We mention here calculations [16] made in studying LTC caused by defects. Such defects are also good candidates for producing the CP in perovskites. However, they are not of central interest here.

We will briefly describe the model and the main results of MCA,and then give a short explanation of our simulation technique and of the physical quantities calculated. The main results are then presented and discussed.

We start by studying the scalar Φ^4-lattice model with NNI:

$$H = \sum_l \left(\frac{P_l^2}{2} - \frac{1}{2} X_l^2 + \frac{1}{4} X_l^4 + \frac{1}{2} f (X_l - X_{l-1})^2 \right). \tag{1}$$

X_l and P_l are canonically conjugate particle displacements and momenta. Index l runs over all unit cells. f is the harmonic interaction constant of nearest neighbours. All variables are dimensionless (see [6]). This model exhibits a SPT of second order at a temperature T_c . For $d = 1$ one has, however, $T_c = 0$ [1, 15].

The mode-coupling approach starts with the Laplace transform

$$S_q(z) = \frac{1}{\mathrm{i}} \int_0^\infty \mathrm{d}t \, \mathrm{e}^{\mathrm{i}zt} S_q(t) \qquad \mathrm{Im}(z) > 0 \qquad \text{with } A_q = \sum_l \mathrm{e}^{\mathrm{i}ql} A_l \tag{2}$$

of the displacement–displacement correlation function

$$S_{lk}(t) = \langle X_l(t) X_k(0) \rangle \tag{3}$$

where the brackets denote thermodynamic averaging for a canonical ensemble.

Using standard Green function equations of motion [17] one obtains

$$S_q(z) = \langle X^2 \rangle_q / \{ z - (T/\langle X^2 \rangle_q) / [z - (1/T) M_q(z)] \} \tag{4}$$

where the structure of the relaxation kernel $M_q(z)$ can be found elsewhere [2, 7, 8]. Using simple factorization procedures within $M_q(z)$ one derives the 'mode-coupling approximation':

$$M_{lk}(t) \approx \gamma S_{lk}^3(t). \tag{5}$$

The parameter γ is usually assumed to be equal to 6 [2]. However, the scenario described below remains qualitatively unchanged if γ is varied (cf [7]).

The equations (4) and (5) can now be solved self-consistently. Using the results of a corresponding schematic F_3-model [5] one can reach the following conclusions.

(1) There can exist non-vanishing long-time correlations

$$L_{lk} = \lim_{t\to\infty} S_{lk}(t). \tag{6}$$

(2) If they exist then there exists some temperature T_g such that for

$$\begin{aligned} T > T_g \qquad & L_{lk} = 0 \\ T \leqslant T_g \qquad & L_{lk} \neq 0. \end{aligned} \tag{7}$$

(3) The dependence on $L_{lk}(T)$ is discontinuous at T_g:

$$L_{lk}(T \longrightarrow T_g - 0) \neq 0. \tag{8}$$

(4) Near T_g ($T < T_g$) the dependence on $L_{lk}(T)$ is given by

$$L_{lk}(T) - L_{lk}(T_g) \sim \sqrt{T_g - T}. \tag{9}$$

(5) Near T_g ($|T - T_g|/T_g \ll 1$) one obtains β- and α-relaxation properties of S (see [5]). The relaxation process we are interested in (L_{lk}) freezes in at T_g, i.e. its time scale

$$t_{T_g} \sim t_0/[(T - T_g)/T_g]^{1/2a+1/2b} \tag{10}$$

diverges as T_g is reached (t_0 is the relevant microscopic time scale and $a > 0$, $b > 0$ are model parameters).

The numerical solution derived in [2] under some additional assumptions agrees with 1–4 whereas property 5 was not under study for model (1).

We now discuss the molecular dynamics technique. In order to obtain thermodynamic properties of model (1)—especially the time dependence of correlation function (3)—we performed MD simulations following [11]. The Langevin equations with Gauss-distributed stochastic forces $F_l(t)$

$$\ddot{X}_l(t) = -\partial H/\partial X_l - \Gamma P_l + F_l(t) \tag{11}$$

$$\int F_l(t)F_k(t+\tau)\,\mathrm{d}t = 2T\Gamma\delta_{lk}\delta(\tau) \tag{12}$$

are solved numerically. The friction constant Γ must obey the inequality

$$\text{characteristic microscopic time} \ll 1/\Gamma \ll \text{simulation period.}$$

We used a Verlet algorithm [11] and the parameters

$$\begin{aligned} &\text{time iteration step, } \Delta t \equiv 0.05 \qquad \Gamma \equiv 10^{-3} \\ &\text{probability of a random pulse} \equiv 0.05 \end{aligned} \tag{13}$$

The equations of motion were solved under periodic boundary conditions. The system sizes under study were $N = 100, 500, 2000, 4000$.

The Fourier transformation of $X_l(t)$ is obtained using a fast Fourier transform [18]. We obtain $S_{ll}(\omega_k)$ at 10^4 ω_k-points. A smoothing of the spectra does not change the area below $S(\omega)$. The final resolution of a low-frequency excitation in ω-space is 2×10^{-2}. Since the LTC in (6) can be described as the integral over the corresponding $\delta(\omega)$-peak in $S(\omega)$, we define L in our computer simulations as the integrated intensity of the central peak component (if it exists and is clearly separated from the dynamical part of the spectrum) of $S(\omega)$:

$$L = \int_{CP} \mathrm{d}\omega \; S_{ll}(\omega). \tag{14}$$

Each run was started with Gauss-distributed momenta P_l ($(1/N)\sum_l P_l^2 = T$) and zero displacements. The first simulation period $T_{eq} = 2000$ was used to reach equilibrium with a large $\Gamma_{eq} = 0.03$. The subsequent simulation time $T_s = 9830.4$ with parameters (13) was used to obtain the time evolution of our system. During this time T_s the deviation from equilibrium was checked by calculating the difference of the the integrated averaged squared momentum and the MD temperature T occurring in (12).

To obtain the Fourier spectrum of the correlation function $S_{ll}(t)$ we use the discrete Wiener–Khinčin theorem [18]:

$$\begin{aligned} &S_{ll}(\omega_k) = |X_l(\omega_k)|^2 \qquad X_l(\omega_k) = \Delta t \sum_{j=0}^{T_s/\Delta t - 1} \mathrm{e}^{-(2\pi \mathrm{i}/T_s)k\,\Delta t\, j} X_l(\Delta t\, j) \\ &\omega_k = \frac{2\pi k}{T_s} \qquad k = -\frac{1}{2}\frac{T_s}{\Delta t}, \ldots, -1, 0, 1, \ldots, \frac{1}{2}\frac{T_s}{\Delta t} - 1. \end{aligned} \tag{15}$$

Besides (14) we also calculated the following thermodynamic quantities: the mean square displacements $\langle X_l^2 \rangle$, the mean cluster length $\langle l \rangle$ (mean length of chain parts with equal sign of particle displacements), the mean constant sign time $\langle \tau \rangle$ of one particle displacement and the FWHM (full width at half maximum) of the central peak component in $S_{ll}(\omega)$.

We tested our simulation technique by using different potentials, e.g. harmonic systems, and found no disagreement with exact results. The main argument supporting our method is, however, the simulation of a system with infinite-range interaction and vanishing interaction strength (because of the use of reduced variables, this corresponds to simply letting $f = 0$ in (1)). For such systems exact results for $\langle X_l^2 \rangle$ and L are known [6]. The data are compared in figure 1. They show perfect agreement for $\langle X_l^2 \rangle$ and good (deviations $\leqslant 10$ per cent) agreement for L. Thus we expect all our numerical procedures to be applicable to the more interesting case of NNI.

We first discuss the qualitative features of the $S(\omega)$-spectra for different ranges of T and f. For weak coupling $f \ll 1$ the spectra exhibit a well defined central peak component and a resonant part (figure 2(a)). This holds for all temperatures except for at the high-T limit. The height of the CP decreases drastically with increasing T whereas the FWHM depends only slightly on T. For coupling constants $f \geqslant 1$ the low-T limit of $S(\omega)$ looks similar to the weakly coupled case. However, an increase

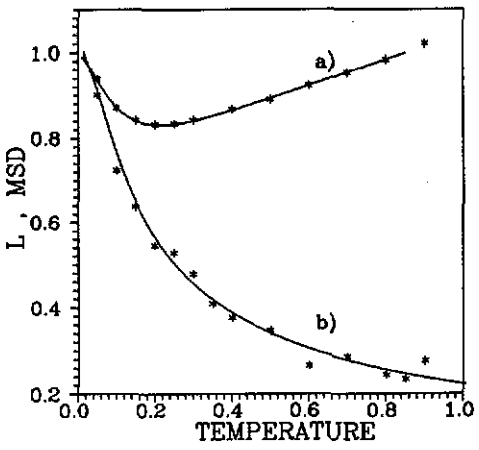

Figure 1. $\langle X_i^2 \rangle$ (a) and L (b) versus temperature for $f=0$. Stars—MD result; solid line—exact result from [6].

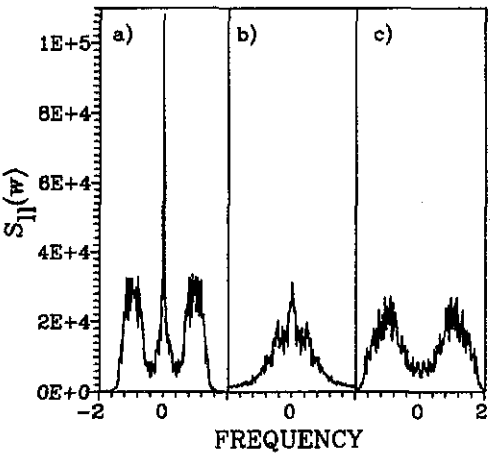

Figure 2. $S_{ll}(w)$-spectra for typical cases. (a) $T=0.7$, $f=0.1$. (b) $T=0.9$, $f=4$. (c) $T=0.9$, $f=0.4$.

of T leads to an additional coalescence of both parts of the spectrum (figure 2(b)). For high enough T the CP component disappears in all cases (figure 2(c)). Varying the interaction strength f for constant temperature, the FWHM shows a maximum at some intermediate value of f and vanishes for vanishing f (this corresponds to the infinite-interaction case) but surprisingly also for high enough f. Except the mean cluster length, all other thermodynamic quantities also exhibit a maximum (or minimum) at the same intermediate value of f. This suggests different origins for the LTC in the case $f \to 0$ (phase space separation) and in the strongly coupled case $f > 1$ (non-linear dynamic behaviour).

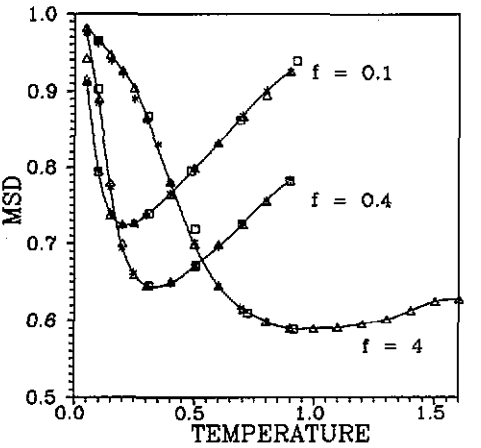

Figure 3. $\langle X_i^2 \rangle$ versus temperature for different coupling strengths f. Triangles—$N=500$; stars—$N=2000$.

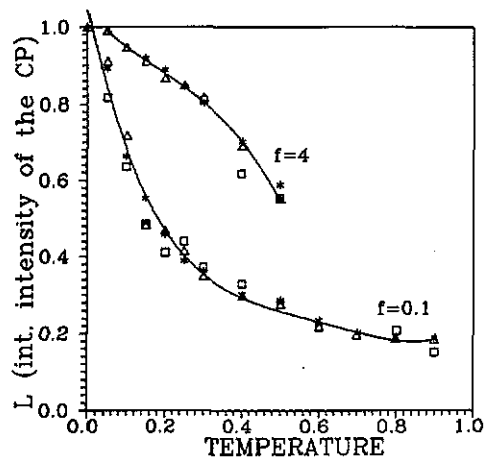

Figure 4. $L(T)$ for $f=0.1$ and $f=4$. Squares—$N=100$; stars—$N=500$; triangles—$N=2000$ (the lines are only guides for the eye).

The mean square displacements as functions of T are shown in figure 3. For weak coupling we obtain nearly the same T-dependence including a minimum at $T \approx 0.2$ as in the case of infinite-range interaction (cf figure 1). With increasing coupling strength the minimum becomes deeper and shifts to higher temperatures in contrast to what is found in the infinite-range interaction case [6].

The calculated integral CP intensities of $S(\omega)$ (according to (14)) are shown in figure 4. For weak coupling, $f \ll 1$, the $L(T)$-curve is similar to the infinite-range interaction result (figure 1), indicating that also for finite, but weak NNI the MCA is unable to explain the temperature dependence of the long-time correlations [7] (no plateau in $L(T) \rightarrow$ no indication of T_g). Increasing the coupling strength changes the situation, however. First of all the curvature of $L(T)$ seems to change its sign. Thus one should expect an $L(T)$-dependence with some plateau. We are unable, however, to determine $L(T)$ at arbitrarily high temperatures due to the above-mentioned coalescence of both the CP and the resonant parts of $S(\omega)$ with increasing T.

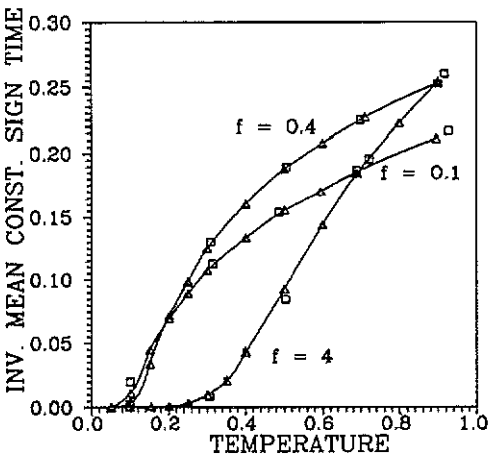

Figure 5. Inverse mean constant sign time $1/\langle\tau\rangle$ versus temperature for different coupling strengths f. Triangles—$N=2000$; stars—$N=4000$.

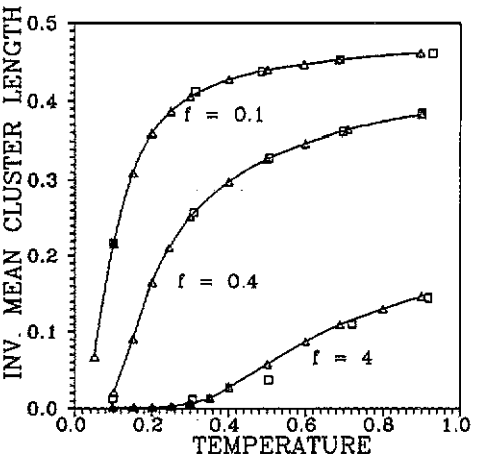

Figure 6. Inverse mean cluster length $1/\langle l\rangle$ versus temperature for different coupling strengths f. Triangles—$N=2000$; stars—$N=4000$.

To decide whether or not some predictions of MCA become true for strong coupling, we plot the inverse mean constant sign time $1/\langle\tau\rangle$ and the inverse mean cluster length $1/\langle l\rangle$ as functions of T (figures 5, 6). We clearly see that for strong coupling there exists a crossover temperature separating temperature regions with different T-dependences of $\langle\tau\rangle$ and $\langle l\rangle$. The dependences on $1/\langle l\rangle$ and $1/\langle\tau\rangle$ in the crossover region are smooth and a fictitious break in the plots occurs only due to the chosen scale of the ordinate. For decreasing coupling this crossover region shifts to lower temperatures. It is interesting to notice that no crossover is seen in the T-dependence of the mean square displacements and thus of the local susceptibilities. No N-dependence of our results was found. Moreover we calculated distributions of cluster lengths and constant sign times for $N=100, \ldots, 4000$ and found identical distribution functions. Thus size effects can be excluded.

Now let us discuss the results. In the case of weak NNI a 1D Φ^4-system behaves similarly to a Φ^4-model with infinite-range interaction not only with respect to the

mean square displacements ($\langle X_l^2 \rangle = \int_{-\infty}^{+\infty} S(\omega)\ \mathrm{d}\omega$) but also with respect to the integrated CP intensity. Thus we conclude, in the same manner as in [7], that in this case MCA does not work for large times in (5) and predictions of MCA fail.

The strong-coupling case exhibits new features: first the $L(T)$-dependence changes its curvature thus making a sharper crossover to small L-values with increasing temperature possible. Secondly we see a crossover in the temperature dependences of $\langle l \rangle$ and $\langle \tau \rangle$. This observed crossover temperature is definitely below the temperature range in which the $L(T)$-crossover is expected. This is not surprising in MCA: assuming the existence of T_g one expects α-relaxation processes for $T \geqslant T_g$ at large times [5] (see property 5, above). This slow α-dynamics is not resolved in the CP by our technique. Thus an evaluation of the $L(T)$-curves obtained by our simulation method should, indeed, yield values for T_g that are too high . To avoid this overestimation one should study the extreme long-time behaviour of $S(t)$.

Summarizing, we conclude that LTC appear in a 1D Φ^4-model due to phase space separation for weak NNI coupling while they seem to have a different origin (e.g. soliton-like solutions of the continuum limit [19]) in the case of strong coupling. Consequently MCA predictions fail in the weak-coupling case while they seem to be more relevant in the strong-coupling case.

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