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Mode-coupling theory for the lattice dynamics of anharmonic crystals: self-consistent damping and the 1d Lennard-Jones chain

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Abstract. We present a self-consistent theory for the dynamical one-phonon structure factor in anharmonic crystals. The theory is the phonon analogue of the mode-coupling theory of liquid dynamics of Götze and his coworkers. Starting point is the lattice dynamics treatment based on the Mori-Zwanzig technique as formulated by Götze and Michel. We apply the theory to the one-dimensional (1d) Lennard-Jones chain and show that the nonlinear mode-coupling equations can be readily solved in the time domain. The vertices entering the equations as input are calculated exactly by a Monte Carlo technique. We compare our findings with molecular dynamics (MD) simulations and the results of other theoretical approaches.

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I. Introduction

Recent neutron scattering measurements of the dynamical structure factor of transition metals in their high-temperature *bcc* phase [1] stimulated anew the interest in theoretically understanding the vibrational properties of strongly anharmonic crystals. The calculation of the dynamical properties of anharmonic crystals is a long-standing problem which received considerable interest in the sixties and early seventies [2–5]. In later times crystalline argon became a test case for anharmonic phonon theories, because molecular-dynamics simulations of Cowley and Nordberg [6] using the Aziz-Chen (AC) potential [7] reproduced both the dispersion and line shapes of the measured one-phonon structure factor [8] quantitatively. Glyde and Smoes [9] used the (static) self-consistent harmonic phonon theory (SCH) plus cubic corrections (SCH+C) while Cowley and Horton [10] applied the renormalized formalism of Horner [5]. By using the AC potential both groups were able to reproduce the experimentally measured dispersion very well up to the melting point. However, for the line shape reasonable agreement with the experiment could not be achieved. Since the AC potential cannot be blamed for the disagreement with experiment the reason must be the inadequate treatment of the self energy.

There have been also attempts to utilize the perturbation-theoretical scheme for a description of the strongly damped phonon spectra of the *bcc* transition metals [11, 12]. In these attempts an empirical pair potential was used the parameters of which were fitted to obtain correct dispersion curves. Using second-order perturbation theory for the self energy, again, the agreement between the calculated and measured line shape was not satisfactory.

As Cowley and Nordberg [6] point out in connection with their argon simulation, the previous perturbative calculations considered only processes, in which the phonon either decays into two undamped phonons, or combines with one existing phonon to produce a third phonon. Therefore the damping function has only two peaks, one at high frequencies and another at low frequencies. If the phonon has a frequency in the gap, the damping is very small. Inclusion of decay processes, in which the phonons decay into more intermediate phonons would broaden the energy dependence. A first attempt to take such processes into account is the so-called second-order self-consistent phonon theory (SC2) [13]. But for solid argon this scheme does not seem to have solutions in the high-temperature regime [14], in contrast to the self-consistent harmonic theory (SCH) which has a good convergence behaviour in this limit.

A further test case for anharmonic theories is the one-dimensional (1d) Lennard-Jones chain with nearest-neighbour interactions. Cuccoli and Tognetti [15] formulated a theory for the one-phonon structure factor for anharmonic crystals up to the melting point, using the Mori-Zwanzig continued-fraction method [16, 17]. They calculated the first six classical moments exactly and terminated the continued fraction by a Gaussian memory function. The resulting spectral functions were compared to a classical MD calculation of the one-phonon structure factor [18].

Freidkin, Horton and Cowley used perturbation theory [19] for an explicit evaluation of the one phonon structure factor for the LJ chain with nearest-neighbour (NN) interaction. They derived an analytic expression for the lowest-order term for the self energy which represents a decay process into two undamped phonons. Their results agree to

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Dedicated to Wolfgang Götze on the occasion of his 60th birthday the MD calculations of Cuccoli et al. [18] only in the low-temperature limit.

The Mori-Zwanzig technique was also applied to a realistic model of argon by Cowley and Zekaria [20]. There, the first five even moments were calculated by a classical Monte Carlo simulation and various methods of terminating the continued fraction expansion for the spectral function were tested. Their result is: When a Gaussian model spectrum [21] for the memory functions is used, the peak center is correctly located and the height and width of the peak of the simulated one-phonon spectrum are reproduced to about 20% accuracy.

The formalism developed by Götze and Michel [4] gives a connection between the Mori-Zwanzig technique and the diagrammatic perturbation theory. It turns out that the second-order memory function is identical to the self energy of the one-phonon structure factor. As compared to the perturbative scheme the Mori-Zwanzig formalism has the advantage that the moment sum rules can be incorporated exactly into the theory.

In the following we present a self-consistent theory for the self energy (memory function) of the one-phonon structure factor. The theory is formulated classically, since we are primarily interested in the high-temperature regime. However the generalisation to the quantum case is straightforward and will be carried out later on.

In the perturbation-theoretical language the theory is obtained by using "dressed" Green's functions in the second-order expression for the self-energy. In the Mori-Zwanzig formalism this is equivalent to performing a mode-coupling approximaton for the phonon propagator. This yields a nonlinear equation for the one-phonon propagator. In one dimension this equation is mathematically identical to the mode-coupling equation used for describing liquid dynamics [22] and especially the liquid-glass transition [23, 24]

In section II we express the equation of motion for the one-phonon propagator in terms of a generalized Bloch-Langevin-equation for the Kubo relaxation function [25, 4]. As in the mode-coupling theory for the glass transition the equation is solved numerically most effectively in the time domain and shows a very good convergence behavior.

The memory kernel with decay into two (damped) phonons is written down classically. We discuss different methods for calculating the static phonon susceptibility and the phonon-phonon-coupling constant as a function of temperature. In section III we apply the theory to the 1d Lennard-Jones chain. In section IV we compare our mode-coupling spectral shapes with those obtained by the mentioned simulations [18] and the continued-fraction method [15].

II. Theory

A. The equation of motion for the phonon correlator

We consider a single crystal in which the atoms are assumed to be distinguistable and obey the equations of motion of classical mechanics. They are labelled by integer vectors $\mathbf{n} = (n_1, n_2, n_3) \quad ; \quad n_i = 0, \pm 1, \pm 2, \cdots \quad .$

The three coordinate directions ($1{=}x$,$2{=}y$,$3{=}z$) are denoted by means of the subscripts i, j, k, l, m, n. The dynamical variables of the system are the deviations $\varphi_i(\mathbf{n})$ of the $\mathbf{n}$th atom in the ith direction from its equilibrium point $\mathbf{X}(\mathbf{n})$ together with the corresponding momentum operator $\pi_i(\mathbf{n})$. The standard expressions for φ_i and π_i in reciprocal space are

$$\varphi_i(\mathbf{q}) = \sqrt{\frac{M}{N}} \sum_{\mathbf{n}} e^{-i\mathbf{q}\mathbf{X}(\mathbf{n})} \, \varphi_i(\mathbf{n}) \tag{1}$$

and

$$\pi_i(\mathbf{q}) = \sqrt{\frac{1}{M\,N}} \sum_{\mathbf{n}} e^{-i\mathbf{q}\mathbf{X}(\mathbf{n})} \, \pi_i(\mathbf{n}) \qquad , \tag{2}$$

were $\mathbf{q}$ denotes a vector in the first BZ, and we have the Poisson brackets

$$\{\varphi_i^\dagger(\mathbf{q}), \pi_j(\mathbf{k})\} = -\delta_{i,j}\delta_{\mathbf{q}.\mathbf{k}} \quad . \tag{3}$$

The Hamiltonian H for the ideal anharmonic bravais crystal is given by

$$H = \frac{1}{2M} \sum_{\mathbf{q}i} \pi_i(\mathbf{q})\, \pi_i(\mathbf{q}) + \sum_{\nu=0}^{\infty} (\frac{1}{\nu!}) \\ \times \sum_{\mathbf{q_1}i_1,\cdots,\mathbf{q}_\nu i_\nu} V(\mathbf{q_1}i_1, \cdots, \mathbf{q}_\nu i_\nu)\, \varphi_{i_1}(\mathbf{q_1}) \cdots \varphi_{i_\nu}(\mathbf{q}_\nu) \ , \tag{4}$$

where M is particle mass. The coupling coefficients are considered to be given.

We consider the six variables $A_\alpha = (\varphi_i(\mathbf{q}), \pi_i(\mathbf{q});\ i = 1, 2, 3)$ as the "slow" variables of the system and denote by $\mathscr{P}$ the projector onto the subspace of these dynamical variables. The correlator $\Phi_{\alpha\beta}(t)$ is defined as a scalar product $(\cdots \mid \cdots)$ in the Hilbert space $\mathscr{H}$ of the dynamical variables $A_\alpha, A_\beta, \cdots$:

$$\Phi_{\alpha\beta}(t) = (A_\alpha(t) \mid A_\beta) = (A_\alpha \mid e^{-i\mathscr{L}\,t} \mid A_\beta) \\ = \frac{1}{k_B T} \langle\, \delta A_\alpha^*(t)\, \delta A_\beta \,\rangle = \frac{1}{k_B T} \langle\, A_\alpha^*(t)\, A_\beta \,\rangle \quad , \tag{5}$$

where $\partial_t A_\alpha(t) = i\mathscr{L} A_\alpha(t) = -i\{H, A_\alpha(t)\}$ is the Liouvillian, and we define $A_\alpha(t = 0) = A_\alpha$. The last equality in (5) follows from $< \varphi_i(\mathbf{n}) >= 0$ and $< \pi_i(\mathbf{n}) >= 0$. The Laplace transform of the matrix $\Phi(t)$ is the resolvent of $\mathscr{L}$ with respect to the "states" A_α:

$$\Phi_{\alpha\beta}(\mathbf{q}, z) = \mp\, i \int_{-\infty}^{\infty} dt \Theta(\pm t)\, e^{izt}\, \Phi_{\alpha\beta}(\mathbf{q}, t) \quad , \quad \Im m\, z \gtrless 0 \\ = (A_\alpha \mid \frac{1}{z - \mathscr{L}} \mid A_\beta).$$

Within the projector formalism of Zwanzig and Mori [17] the resolvent is now expressed in terms of a matrix $M(\mathbf{q}, z)$ of relaxation kernels (memory functions) $M_{\alpha\beta}(\mathbf{q}, z)$, the restoring force matrix $\Omega(\mathbf{q})$, and the static susceptibility matrix $\chi^0(\mathbf{q})$ in the following way:

$$[z\mathbf{1} - \Omega(\mathbf{q}) + M(\mathbf{q}, z)]\, \Phi(\mathbf{q}, z) = \chi^0(\mathbf{q}) \quad , \tag{6}$$

where $\mathbf{1}$ is the 6×6 unit matrix. The matrix $\chi^0(\mathbf{q})$ can be calculated by using the Yvon theorem $(A_\alpha \mid \mathscr{L} \mid A_\beta) = -i \,\langle\, \{A_\alpha^*, A_\beta\, \}\,\rangle$:

$$\chi^0_{\alpha\beta}(\mathbf{q}) = (A_\alpha(\mathbf{q})|A_\beta(\mathbf{q})) = \begin{pmatrix} \tilde{D}^{-1}(\mathbf{q}) & 0 \\ 0 & \tilde{\mathbf{1}} \end{pmatrix}_{\alpha\beta} \quad . \tag{7}$$

$\tilde{\mathbf{1}}$ is the 3×3 unit matrix and $\tilde{D}(\mathbf{q})$ is defined by

$$
\begin{aligned}
D_{ij}^{-1}(\mathbf{q}) = (\,\varphi_i(\mathbf{q}) \mid \varphi_j(\mathbf{q})\,) \;=\; \frac{1}{k_BT}\,\langle\,\varphi_i^*(\mathbf{q})\,\varphi_j(\mathbf{q})\,\rangle \\
= \Phi_{ij}^{\varphi\varphi}(\mathbf{q}, t=0).
\end{aligned}
\tag{8}
$$

Since $\tilde{D}(\mathbf{q})$ is a hermitian positive matrix it can be written as

$$
D_{ij}(\mathbf{q}) \;=\; \sum_{\alpha=1}^{3}\, e_i(\mathbf{q},\alpha)\,\omega^2(\mathbf{q},\alpha)\,e_j^*(\mathbf{q},\alpha),
\tag{9}
$$

where $\omega(\mathbf{q},\alpha)$ are the phonon frequencies and $e_i(\mathbf{q},\alpha)$ the polarisation vectors. The restoring force matrix is defined by $\Omega = \omega\,(\chi^0)^{-1}$, with $\omega_{\alpha\beta} = (A_\alpha \mid \mathscr{L} \mid A_\beta)$ and is explicitly given by

$$
\Omega(\mathbf{q}) = \begin{pmatrix} 0 & -i\tilde{\mathbf{1}} \\ i\,\tilde{D}(\mathbf{q}) & 0 \end{pmatrix} \quad .
\tag{10}
$$

Finally, the memory function matrix has the representation

$$
M(\mathbf{q},z) \;=\; m(\mathbf{q},z)\,(\chi^0)^{-1} \;=\; \begin{pmatrix} 0 & 0 \\ 0 & \tilde{P}(\mathbf{q},z) \end{pmatrix}
\tag{11}
$$

with

$$
m_{\alpha\beta}(\mathbf{q},z) \;=\; (\mathscr{Q}\mathscr{L}\,A_\alpha(\mathbf{q}) \,|\, \mathscr{R}_{\mathscr{Q}} \,|\, \mathscr{Q}\mathscr{L}\,A_\beta(\mathbf{q}))
\tag{12}
$$

where $\mathscr{Q} = \mathbf{1} - \mathscr{P}$ projects rectangular to the variables A_α, and $\mathscr{R}_{\mathscr{Q}} = [z - \mathscr{Q}\mathscr{L}\mathscr{Q}]^{-1}$. $\tilde{P}(\mathbf{q},z)$ is the 3×3 - matrix

$$
P_{ij}(\mathbf{q},z) \;=\; (\mathscr{Q}\mathscr{L}\,\pi_i(\mathbf{q}) \,|\, \mathscr{R}_{\mathscr{Q}} \,|\, \mathscr{Q}\mathscr{L}\,\pi_j(\mathbf{q})) \quad .
\tag{13}
$$

For the displacement–displacement correlator matrix $\tilde{\Phi}^{\varphi\varphi}(\mathbf{q},z)$ equation (6) now reduces to the 3×3 matrix equation:

$$
\begin{aligned}
z^2\,\tilde{\Phi}^{\varphi\varphi}(\mathbf{q},z) \;-\; z\,\tilde{D}^{-1}(\mathbf{q}) \;-\; \tilde{D}(\mathbf{q})\,\tilde{\Phi}^{\varphi\varphi}(\mathbf{q},z) \\
+\,\tilde{P}(\mathbf{q},z)\,\left(\,z\,\tilde{\Phi}^{\varphi\varphi}(\mathbf{q},z) \;-\; \tilde{D}^{-1}(\mathbf{q})\,\right) \;=\; 0 \quad .
\end{aligned}
\tag{14}
$$

Transforming back into the time regime we obtain the following equation of motion for the phonon correlator:

$$
\begin{aligned}
\ddot{\tilde{\Phi}}^{\varphi\varphi}(\mathbf{q},t) \;+\; \tilde{D}(\mathbf{q})\,\tilde{\Phi}^{\varphi\varphi}(\mathbf{q},t) \\
+\int_0^t \mathrm{d}t'\;\tilde{P}(\mathbf{q},t-t')\,\dot{\tilde{\Phi}}^{\varphi\varphi}(\mathbf{q},t') \;=0
\end{aligned}
\tag{15}
$$

$$
\tilde{\Phi}^{\varphi\varphi}(\mathbf{q},t=0) \;=\; \tilde{D}^{-1}(\mathbf{q}), \qquad \dot{\tilde{\Phi}}^{\varphi\varphi}(\mathbf{q},t=0) \;=\; 0,
\tag{16}
$$

which is a generalized Bloch-Langevin-equation. This equation allows for an interpretation as a system of oscillators, coupled by a generalized friction term.

B. The mode coupling approach

Until now only exact rearrangements have been performed. The nontrivial task is to find explicit expressions for the static phonon susceptibility $\tilde{D}(\mathbf{q})$ and the relaxation kernel $\tilde{P}(\mathbf{q},t)$. In the previous literature for both quantities perturbation theory has been used. In phonon theories for $\tilde{D}(\mathbf{q})$ the approximate expressions have very often the following structure [4] :

$$
\begin{aligned}
D_{ij}(\mathbf{q}) = D_{ij}^{(0)}(\mathbf{q}) \\
+\frac{k_BT}{2}\sum_{\mathbf{q}_1,\alpha_1}\frac{V(\mathbf{q}i,-\mathbf{q}j,\mathbf{q}_1k,-\mathbf{q}_1l)e_k(\mathbf{q}_1,\alpha_1)e_l^*(\mathbf{q}_1,\alpha_1)}{\omega^2(\mathbf{q}_1,\alpha_1)} \\
-\frac{k_BT}{2}\sum_{\substack{\mathbf{q}_1,\mathbf{q}_2\\ \alpha_1\alpha_2}}\sum_{i_1\cdots i_4}\frac{V(\mathbf{q}i,-\mathbf{q}_1i_1,-\mathbf{q}_2i_2)e_{i_1}^*(\mathbf{q}_1,\alpha_1)e_{i_2}^*(\mathbf{q}_2,\alpha_2)}{\omega^2(\mathbf{q}_1,\alpha_1)} \\
\times\frac{V(-\mathbf{q}j,\mathbf{q}_1i_3,\mathbf{q}_2i_4)e_{i_3}(\mathbf{q}_1,\alpha_1)e_{i_4}(\mathbf{q}_2,\alpha_2)}{\omega^2(\mathbf{q}_2,\alpha_2)}
\end{aligned}
\tag{17}
$$

For $D_{ij}^{(0)}(\mathbf{q})$ there are different renormalisation procedures like the self–consistent harmonic phonon theory (SCH) [13] or the Horner approximation [5]. The remaining corrections on the right-hand side of equation (17) are then calculated with the frequencies $\omega(\mathbf{q},\alpha)$, that correspond to $D_{ij}^{(0)}(\mathbf{q})$ via Eq. (9).

The mode–coupling scheme has the advantage that the static and dynamic aspects are decoupled, so that one can use, if possible, exact expressions for the static quantities as input for the approximate calculation of the relaxation kernel.

Following Götze and Michel [4] we define a renormalized harmonic Hamiltonian in which the bare force constants are replaced by the correlation function $D_{ij}(\mathbf{q})$:

$$
H_0 \;=\; \frac{1}{2}\sum_{\mathbf{q},i}\,\pi_i^\dagger(\mathbf{q})\,\pi_i(\mathbf{q}) \;+\; \frac{1}{2}\sum_{\mathbf{q},i,j}\,\varphi_i^\dagger(\mathbf{q})\,D_{ij}(\mathbf{q})\,\varphi_j(\mathbf{q})
\tag{18}
$$

and write the crystal Hamiltonian as $H \;=\; H_0 \;+\; H'$ and, correspondingly, $\mathscr{L} \;=\; \mathscr{L}_0 \;+\; \mathscr{L}'$. We obtain

$$
\mathscr{L}_0\varphi_i(\mathbf{q}) \;=\; i\,\pi_i(\mathbf{q}) \qquad \mathscr{L}_0\pi_i(\mathbf{q}) \;=\; -i\,D_{ij}(\mathbf{q})\,\varphi_j(\mathbf{q})
\tag{19}
$$

$$
\mathscr{L}'\varphi_i(\mathbf{q}) \;=\; 0 \qquad \mathscr{L}'\pi_i(\mathbf{q}) \;=\; -i\,\rho(\mathbf{q}i)
\tag{20}
$$

For the system H_0 one finds $\mathscr{Q}\mathscr{L}_0\pi_i(\mathbf{q}) \;=\; 0$ and therefore $P_{ij}(\mathbf{q},t) \;=\; 0$. The operator $\mathscr{L}_0$ describes the motion of statically renormalized non-interacting phonons, and $\mathscr{L}'$ describes the interaction. The operator $\rho(\mathbf{q}\;i)$ obeys $\rho^\dagger(\mathbf{q}\;i) \;=\; \rho(-\mathbf{q}\;i)$ and has the explicit form

$$
\begin{aligned}
\rho(\mathbf{q}\;i) \;=\; \sum_{\nu=0}^{\infty}\left(\frac{1}{\nu!}\right)\sum_{\mathbf{q_1}i_1,\cdots,\mathbf{q}_\nu i_\nu} V'(\mathbf{q}i,\mathbf{q_1}i_1,\cdots,\mathbf{q}_\nu i_\nu) \\
\times\varphi_{i_1}^\dagger(\mathbf{q_1})\cdots\varphi_{i_\nu}^\dagger(\mathbf{q}_\nu)
\end{aligned}
\tag{21}
$$

with

$$
\begin{aligned}
V'(\mathbf{q}i,\mathbf{q_1}i_1,\cdots,\mathbf{q}_\nu i_\nu) \;=\; V(\mathbf{q}i,\mathbf{q_1}i_1,\cdots,\mathbf{q}_\nu i_\nu) \\
\text{if}\quad \nu \neq 1, \\
V'(\mathbf{q}i,-\mathbf{q}j) \;=\; V(\mathbf{q}i,-\mathbf{q}j) \;-\; D(\mathbf{q}i,-\mathbf{q}j\,).
\end{aligned}
\tag{22}
$$

In a next step we introduce cumulant products of displacement operators by defining

$$
\begin{aligned}
(\varphi_{i_1}(\mathbf{q_1})\,\cdots\,\varphi_{i_\nu}(\mathbf{q}_\nu))_c \;=\; \varphi_{i_1}(\mathbf{q_1})\,\cdots\,\varphi_{i_\nu}(\mathbf{q}_\nu) \\
-\sum_{\mathbf{q}_{\mu_1}\mu_1}^{\nu}\,\varphi_{i_{\mu_1}}(\mathbf{q}_{\mu_1})\,\langle\,\varphi_{i_1}(\mathbf{q_1})\,\cdots\,\cancel{\varphi}_{i_{\mu_1}}(\mathbf{q}_{\mu_1})\,\cdots\,\varphi_{i_\nu}(\mathbf{q}_\nu)\,\rangle \\
-\frac{1}{2!}\sum_{\substack{\mathbf{q}_{\mu_1},\mathbf{q}_{\mu_2}\\ i_{\mu_1},i_{\mu_2}}}^{\nu}(\,\varphi_{i_{\mu_1}}(\mathbf{q}_{\mu_1})\,\varphi_{i_{\mu_2}}(\mathbf{q}_{\mu_2})\,)_c\,\langle\,\varphi_{i_1}(\mathbf{q_1})\,\cdots \\
\cdots\,\cancel{\varphi}_{i_{\mu_1}}(\mathbf{q}_{\mu_1})\,\cdots\,\cancel{\varphi}_{i_{\mu_2}}(\mathbf{q}_{\mu_2})\,\cdots\,\varphi_{i_\nu}(\mathbf{q}_\nu)\,\rangle \;+\;\cdots
\end{aligned}
\tag{23}
$$

where $\cancel{\varphi}_{i_{\mu_1}}(\mathbf{q}_{\mu_1})$ means that in the correlation function $\varphi_{i_{\mu_1}}(\mathbf{q}_{\mu_1})$ is missing.
An important relation for later calculations is [4]

$$\langle \{ \left(\varphi_{i_1}(\mathbf{q}_1) \cdots \varphi_{i_\nu}(\mathbf{q}_\nu) \right)_c \, , \, \pi_j(\mathbf{k}) \} \rangle = 0 \quad \text{for } \nu \geq 2 \quad .(24)$$

The phonon self-energy kernels (13) are the Laplace transforms of the fluctuating force correlators

$$P_{ij}(\mathbf{q}, t) = (\mathscr{F}_i(\mathbf{q}) \mid \exp(-i\mathscr{QLQ}\, t) \mid \mathscr{F}_j(\mathbf{q})) \, , \\ \mathscr{F}_j(\mathbf{q}) = \mathscr{QL}\, \pi_j(\mathbf{q}) \, . \qquad (25)$$

The *first* step in the mode–coupling approximation now consists in projecting the fluctuating force $\mathscr{F}$ onto the subspace of the displacement-displacement fluctuations. This is achieved by the projector

$$\mathscr{P}_{(\varphi\varphi)} = \frac{1}{2!} \sum_{\substack{\mathbf{q}_1\mathbf{q}_2 \; \mathbf{q}_1 \neq \mathbf{q}_2 \\ i_1 i_2 i_3 i_4}} \frac{\mid (\varphi_{i_1}(\mathbf{q}_1)\varphi_{i_2}(\mathbf{q}_2))_c \,)\, (\, (\varphi_{i_3}(\mathbf{q}_1)\varphi_{i_4}(\mathbf{q}_2))_c \mid}{(\, (\varphi_{i_1}(\mathbf{q}_1)\varphi_{i_2}(\mathbf{q}_2))_c \mid (\varphi_{i_3}(\mathbf{q}_1)\varphi_{i_4}(\mathbf{q}_2))_c \,)} \qquad (26)$$

leading to

$$P_{ij}(\mathbf{q}) \approx (\mathscr{F}_i(\mathbf{q})\mathscr{P}_{(\varphi\varphi)} | \exp(-i\mathscr{QLQ}\,t) | \mathscr{P}_{(\varphi\varphi)}\mathscr{F}_j(\mathbf{q})) \quad .(27)$$

We now perform the *second* and main step:
Averages of products, evolving in time with generator $\mathscr{QLQ}$ are factorized into products of averages, formed with variables evolving in time with generator $\mathscr{L}$:

$$\begin{aligned} &(\, (\varphi_{i_1}(\mathbf{q_1})\varphi_{i_2}(\mathbf{q_2}))_c \mid \exp(-i\mathscr{QLQ}\; t) \mid (\varphi_{i_3}(\mathbf{q_3})\varphi_{i_4}(\mathbf{q_4}))_c \,) \\ &\quad \approx \frac{1}{k_B T} \left[\langle\, \varphi^*_{i_1}(\mathbf{q_1}, t)\varphi_{i_3}(\mathbf{q_3}) \,\rangle \langle\, \varphi^*_{i_2}(\mathbf{q_2}, \mathbf{t})\varphi_{i_4}(\mathbf{q_4}) \,\rangle \right. \\ &\qquad \left. + \langle\, \varphi^*_{i_1}(\mathbf{q_1}, t)\varphi_{i_4}(\mathbf{q_4}) \,\rangle \langle\, \varphi^*_{i_2}(\mathbf{q_2}, \mathbf{t})\varphi_{i_3}(\mathbf{q_3}) \,\rangle \right] \\ &\qquad = k_B T \left[\Phi^{\varphi\varphi}_{i_1 i_3}(\mathbf{q}_1, t)\, \Phi^{\varphi\varphi}_{i_2 i_4}(\mathbf{q}_2, t)\, \delta_{\mathbf{q}_1\mathbf{q}_3}\, \delta_{\mathbf{q}_2\mathbf{q}_4} \right. \\ &\qquad\quad \left. + \Phi^{\varphi\varphi}_{i_1 i_4}(\mathbf{q}_1, t)\, \Phi^{\varphi\varphi}_{i_2 i_3}(\mathbf{q}_2, t)\, \delta_{\mathbf{q}_1\mathbf{q}_4}\, \delta_{\mathbf{q}_2\mathbf{q}_3} \right] \quad . \end{aligned} \qquad (28)$$

For $t = 0$ this result can be used to calculate:

$$(\, (\varphi_{i_1}(\mathbf{q}_1)\varphi_{i_2}(\mathbf{q}_2))_c \mid (\varphi_{i_3}(\mathbf{q}_1)\varphi_{i_4}(\mathbf{q}_2))_c \,)^{-1} \qquad (29) \\ = \frac{1}{k_B T} D_{i_1 i_3}(\mathbf{q}_1)\, D_{i_2 i_4}(\mathbf{q}_2) \quad \text{for} \quad \mathbf{q}_1 \neq \mathbf{q}_2 \, .$$

Now it is necessary to determine $(\mathscr{F}_i(\mathbf{q}) | (\varphi_{i_1}(\mathbf{q_1})\varphi_{i_2}(\mathbf{q_2}))_c)$. There are two terms contributing: the first one is $(\mathscr{L}\pi_i(\mathbf{q}) \; |(\varphi_{i_1}(\mathbf{q_1})\varphi_{i_2}(\mathbf{q_2}))_c)$. This term is zero, which follows from the Yvon theorem and equation (24). This is different from what holds in the problem of liquid dynamics, where one is interested in the density fluctuations [23]. In the liquid problem the main part of the vertex comes from this term. In our case the main contribution comes from the second term, which can calculated by means of the projector $\mathscr{P}$, the Yvon theorem and equation (3): $\mathscr{PL}\pi_i(\mathbf{q}) = i \sum_j \varphi_j(\mathbf{q})D_{ji}(\mathbf{q})$. Therefore:

$$\begin{aligned} &(\, \mathscr{F}_i(\mathbf{q}) \mid (\varphi_{i_1}(\mathbf{q_1})\varphi_{i_2}(\mathbf{q_2}))_c \,) \\ &\quad = i \sum_j \left(\, \varphi_j(\mathbf{q}) \mid (\varphi_{i_1}(\mathbf{q_1})\varphi_{i_2}(\mathbf{q_2}))_c \,\right) D_{ji}(\mathbf{q}) \\ &\quad = \frac{i}{k_B T} \sum_j \langle\, \varphi^*_j(\mathbf{q})\, (\varphi_{i_1}(\mathbf{q_1})\varphi_{i_2}(\mathbf{q_2}))_c \,\rangle\, D_{ji}(\mathbf{q}) \quad . \end{aligned} \qquad (30)$$

Now it is useful to define a new vertex

$$V(\mathbf{q}i, \mathbf{q}_1 i_1, \mathbf{q}_2 i_2) = \left(\frac{1}{k_B T}\right)^2 \sum_{j, j_1 j_2} \langle \varphi_j(\mathbf{q})(\varphi_{j_1}(\mathbf{q_1})\varphi_{j_2}(\mathbf{q_2}))_c \rangle \\ \times D_{ij}(\mathbf{q}) D_{i_1 j_1}(\mathbf{q_1}) D_{i_2 j_2}(\mathbf{q_2}). \qquad (31)$$

For small anharmonicity, which means low temperature, it is equal to the bare cubic vertex. Summarizing the results of equations (28), (29) , (30) and (31), inserted into (27), we have:

$$P_{ij}(\mathbf{q}, t) \approx \frac{k_B T}{2} \sum_{\substack{\mathbf{q}_1\mathbf{q}_2 \\ i_1 \cdots i_4}} V(\mathbf{q}i, -\mathbf{q}_1 i_1, -\mathbf{q}_2 i_2)\, \Phi_{i_1 i_3}(\mathbf{q}_1, t) \\ \times \Phi_{i_2 i_4}(\mathbf{q}_2, t) V(-\mathbf{q}j, \mathbf{q}_1 i_3, \mathbf{q}_2 i_4). \qquad (32)$$

The two contributions arising in equation (28), are equal, so we get a prefactor of $2\frac{1}{2!}\frac{1}{2!} = \frac{1}{2}$.

This result is equal to the leading self–energy diagram in *renormalized* pertubation theory [3, 5], which produces a nonvanishing damping. In the previous literature dealing with phonon damping by anharmonic effects the full propagators in the diagram are replaced by *bare* ones. To our opinion, using the *dressed* propagators $\Phi_{i_1 i_2}(\mathbf{q}, t)$ is an important step to properly establish the coupling between one- and two-phonon modes.

In fact, it has been pointed out by Horner [26] that in strongly anharmonic crystals the coupling between one- and two-phonon modes plays a crucial role. It can be visualized by an interplay between displacements and the width of the statistical distribution of the atoms. This coupling, which is established via the vertex function $V(\mathbf{q}_1 i_1, \mathbf{q}_2 i_2, \mathbf{q}_3 i_3)$ does not only give rise to the dominant contribution to the phonon damping, but also leads to the appearance of 1–2 phonon interference terms in the density fluctuation spectrum of the anharmonic crystal.

III. Application to the Lennard-Jones chain

A. One-dimensional mode-coupling equation

For a first application of the phonon version of the mode-coupling approximation we choose as a most simple system the 1d Lennard-Jones (LJ) chain with nearest-neighbour interaction. As mentioned in the introduction this system has been studied already both by various approximation schemes [15, 19] as well as by molecular-dynamics calculations [18]. The interaction potential is $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ [27]. The equilibrium nearest-neighbour distance is $a = [2]^{1/6}\sigma$. In one dimension the mode-coupling matrix equation (15) becomes an ordinary equation for $\phi_q(t)$, which is normalized as $\phi_q(t) = \phi_q(t=0)d_q(t) = d_q(t)/D(q)$. The 1d memory function is given in mode-coupling approximation by equation (32) as

$$P_q(t) = \frac{k_B T}{2} \sum_{q_1, q_2} |V(q, -q_1, -q_2)|^2\, D(q_1)^{-1}\, D(q_2)^{-1} \\ \times d_{q_1}(t)\, d_{q_2}(t)\, \Delta(q + q_1 + q_2), \qquad (33)$$

where

$$V(q, q_1, q_2) = \left(\frac{1}{k_B T}\right)^2 \langle\, \varphi_q \varphi_{q_1} \varphi_{q_2} \,\rangle\, D(q)\, D(q_1)\, D(q_2) \, , (34)$$

and $\Delta = 1$ whenever $q + q_1 + q_2 = G$, a reciprocal-lattice vector. The quantities $D(q)$ and $V(q, -q_1, -q_2)$, defined by equation (8) and (31) can be (and has been) calculated by means of a Monte-Carlo (MC) simulation using the Metropolis algorithm.

Because only nearest–neighbour interactions are taken into account the q dependence of the renormalized force constants is the same as that of the unrenormalized ones. Therefore the static phonon susceptibility $D(q)$ as well as the vertex $V(q, -q_1, -q_2)$ can be written in a similar fashion as the corresponding harmonic quantities (see below or, for example, [28]) with effective quadratic and cubic force constants $< V2 >$,$< V3 >$, resp. :

$$D(q) = 4 < V2 > \sin^2(qa/2), \tag{35}$$

and

$$V(q, q_1, q_2) = (i\,2)^3 < V3 > \sin(qa/2)\sin(q_1a/2) \times \sin(q_2a/2)\, e^{i(q+q_1+q_2)a/2} \Delta(q + q_1 + q_2)\ . \tag{36}$$

In the following the static susceptibilities $D(q)$ are always expressed in the form

$$D(q) = \Omega_q^2 = \Omega_m^2 \sin^2(qa/2) \tag{37}$$

with $(\Omega_m)^2 = 4 < V2 >$. It turns out that the effective vertex in front of the propagators in equation (33) is proportional to $D(q)$ with a q independent proportionality constant

$$\alpha = \frac{k_BT}{2} |V(q, -q_1, -q_2)|^2 D(q)^{-1} D(q_1)^{-1} D(q_2)^{-1} = \frac{1}{2} \frac{< V3 >^2}{< V2 >^3} k_BT \quad . \tag{38}$$

We call α the anharmonic coupling parameter. The mode-coupling equations for the 1d LJ chain with nearest-neighbour interaction can now be written as

$$\ddot{d}_q(t) + \Omega_q^2 d_q(t) + \int_0^t \mathrm{d}t' \; P_q(t - t')\, \dot{d}_q(t') = 0 \tag{39}$$

$$d_q(t = 0) = 1 \quad , \quad \dot{d}_q(t = 0) = 0$$

$$P_q(t) = \Omega_q^2 \alpha \sum_{q_1, q_2} d_{q_1}(t) d_{q_2}(t) \Delta(q + q_1 + q_2). \tag{40}$$

This self consistent pair of equations is essentally the same as that used in the mode-coupling theory for the description of the liquid-glass transition in liquid dynamics [23] , where $d_q(t)$ is replaced by the density relaxator.

The experimentally relevant quantity is the normalized one–phonon structure factor $F_q(\omega)$ [29] which is obtained by Fourier transforming $d_q(t)$, i. e. $F_q(\omega) = -\frac{1}{\pi}\mathcal{I}m\{d_q(\omega + i\epsilon)\}$ where $d_q(z) = \phi_q(z)\, D(q)$.

B. Discussion of the static input parameters

To make contact to approximation schemes used previously and to get a feeling of the influence of the static vertices on the results we used not only the simulated results but also the expressions obtained in SCH and by the Horner ansatz [10].

In Fig. 1 we compare the results for $< V3 >$ of the MC simulation with those of the approximations as a function of temperature. The differences are quite significant (note, however, the suppressed origin of the ordinate).

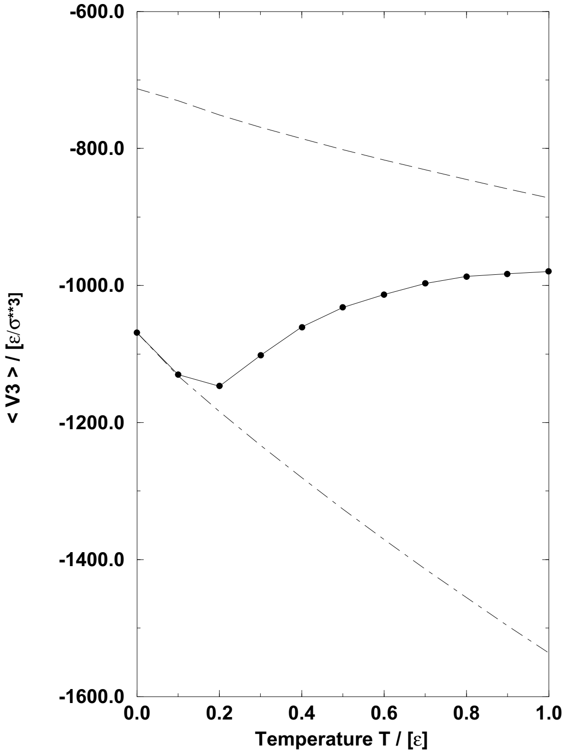

Fig. 1. Third order force constants for different phonon theories vs. temperature. Full line: Monte-Carlo simulation. Dash-dotted line: SCH, dashed line: Horner approximation

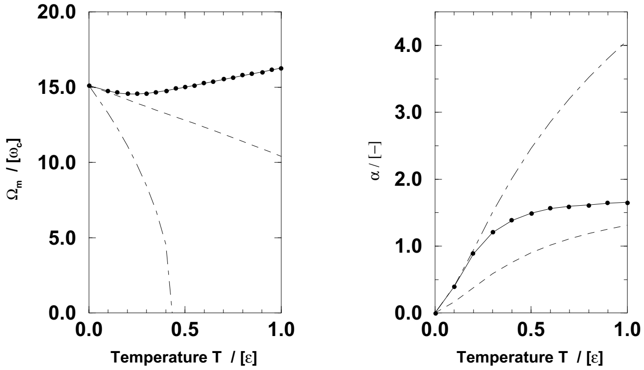

Fig. 2. The two input parameters for the mode-coupling theory, namely the frequency Ω_m and the anharmonic coupling paramter α, are shown for different phonon theories vs. temperature. Symbols are as in Fig. 1. In $\alpha_{SCH/HA}$ only $< V3 >$ is calculated in SCH or Horner approximation, whereas for $< V2 >$ the Monte-Carlo method has always been taken

At $k_BT = 1.0\epsilon$ the value of the cubic force constant using Horner's method is roughly 60 % of the SCH value and $\approx$ 80 % of the bare vertex. These ratios are similar to those in calculations for 3d argon at $T = 82^oK$ [10]. It is also remarkable that the Horner $< V3 >$ does not yield the harmonic result for $T \rightarrow 0^1$.

The relationship between the "smeared" force constants and the phonon frequencies $\Omega_q^{SCH/HA}$ is given by:

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[1] The short-range correlation term approaches zero as $T \rightarrow 0$. The usual cubic contribution is smaller than the corresponding SCH term, because the effective potential $W(r)$ [10] is more symmetric than the LJ potential. This could be a speciality of the one-dimensional system

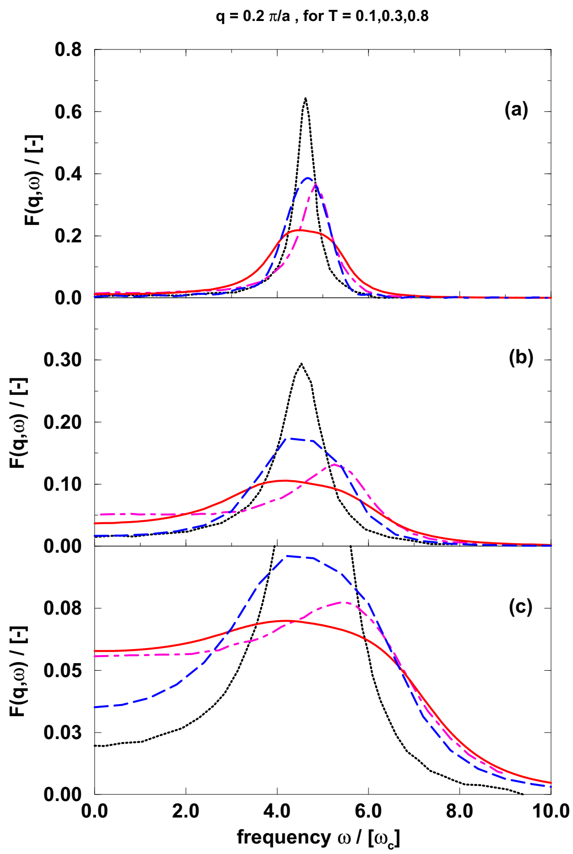

Fig. 3. The one phonon structur factor of the Lennard–Jones chain at $q = 0.2\pi/a$ and **a** $k_BT/\epsilon = 0.1$, **b** $k_BT/\epsilon = 0.3$, and **c** $k_BT/\epsilon = 0.8$. Full line: mode-coupling calculation with Ω_m and α calculated by Monte-Carlo; dashed line: mode-coupling calculation with Ω_m and $< V2 >$ calculated by Monte-Carlo, but $< V3 >$ in Horner approximation. Dot–dashed lines: molecular dynamics results[18]; dotted lines: continued fraction function approach [15]

$$(\Omega_m^{SCH/HA})^2 = 4 \ < V2 >_{SCH/HA} \times \left[1 - \frac{1}{2} k_B T \frac{(< V3 >_{SCH/HA})^2}{(< V2 >_{SCH/HA})^3} \right] . \quad (41)$$

There is no explicit quartic contribution because the quartic terms are contained in the renormalisation of $< V2 >$. In Fig. 2a we show the input parameter Ω_m for the mode-coupling equations, as a function of temperature. Because $\Omega_m^{SCH/HA}$ contains high powers of $< V2 >$ and $< V3 >$ the differences of the approximate quantities from the exact ones are much more drastic. The SCH predicts an instability for the LJ chain above $T \approx 0.45$. The reason is the very large value of the cubic force constant which enters the renormalized frequencies (41) . The phonon frequency of the Horner theory decreases with temperature, the exact one, as calculated by Monte Carlo increases with temperature. Since the second moment of $d_q(\omega)$ is represented poorly by these approximate theories we decided to use only the Monte-Carlo results for Ω_q in our self-consistent calculation of the dynamical one-phonon quantities.

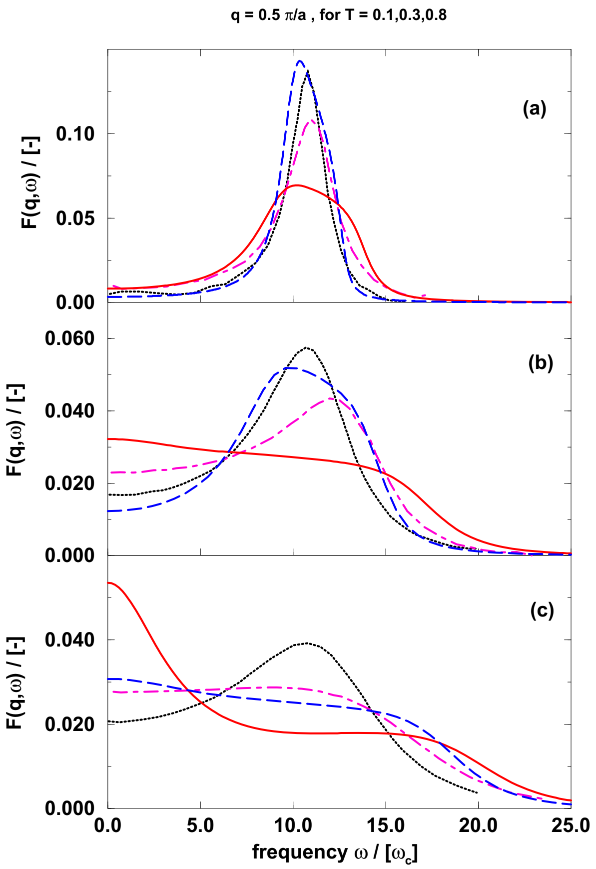

Fig. 4. Same as in Fig. 3 with parameters $q = 0.5\pi/a$ and **a** $k_BT/\epsilon = 0.1$, **b** $k_BT/\epsilon = 0.3$, and **c** $k_BT/\epsilon = 0.8$

In Fig. 2b we compare the approximate coupling constants, which are obtained by using SCH and Horner approximation for $< V3 >$

$$\alpha_{SCH/HA} = \frac{1}{2} k_B T \frac{(< V3 >_{SCH/HA})^2}{(< V2 >)^3} , \quad (42)$$

with the exact one.

Since the SCH coupling is unrealistically large we used only the Horner approximation and the Monte-Carlo results for $< V3 >$ in our mode-coupling calculations.

C. Discussion of the spectra

In Figs. 3 to 5 we show the results for $F(\omega)$ as calculated from (39) and (40) with the exact and the Horner coupling for various temperatures and q values. We compare these curves with the one-phonon structure factor obtained by the MD simulation [18] and the continued-fraction (CF) approach [15]. For small wavenumber ($q = 0.2\pi/a$) we obtain for all temperatures stronger damping than the CF calculation. However the peak positions and widths do not agree with the simulated one. For all values of T and q our results tend to predict too small phonon peaks. It is interesting to note that the results with the Horner coupling agree better to the simulation than those with the exact coupling. This must be due to a cancellation of the errors made by performing

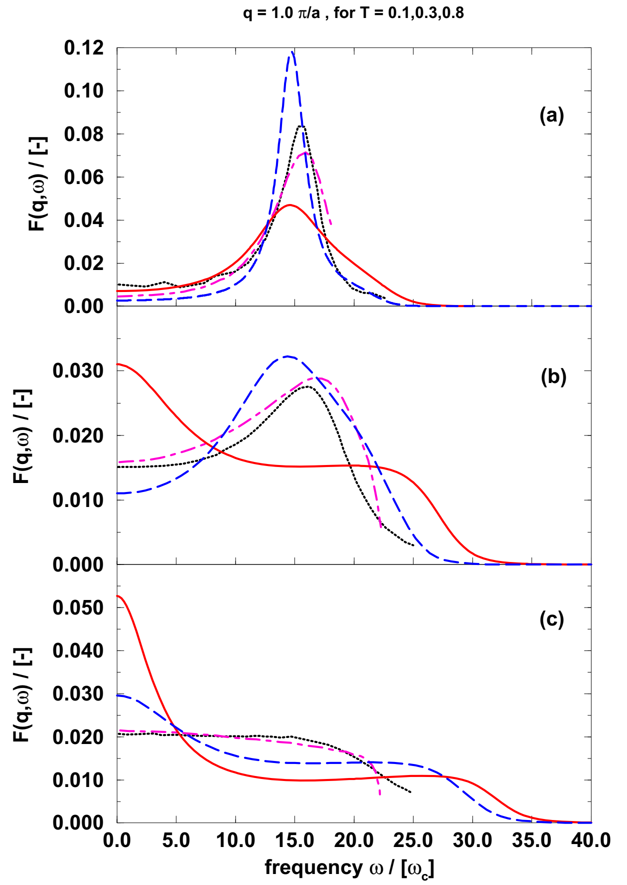

Fig. 5. Same as in Fig. 3 with parameters $q = 1.0\pi/a$ and **a** $k_BT/\epsilon = 0.1$, **b** $k_BT/\epsilon = 0.3$, and **c** $k_BT/\epsilon = 0.8$

the mode-coupling approximation and the Horner approximation. The mode coupling approximation in the present form appears to overestimate the role of the anharmonic interaction. This is probably so, because in the present version the fourth moment sum rule is not obeyed. However, this can be achieved straightforwardly and will be done by us in the future. Our final goal is, however, to use the theory for three–dimensional systems as formulated in Sect. 3.

In conclusion we have presented a self-consistent theory (mode-coupling theory) for the damping of anharmonic lattice vibrations in solids. In contrast to the previous theories using perturbation theory our approach can be applied for strongly anharmonic systems, e. g. solids below their melting points. Applying our theory to the one-dimensional LJ chain we find that the mode-coupling theory overestimates the anharmonic coupling. However the results are in fair agreement with the results of the MD simulation.

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