

Path integral computation of phonon anharmonicity

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Abstract. The partition function of an oscillator disturbed by a set of electron particle paths has been computed by a path integral formalism which permits to evaluate at any temperature the relevant cumulant terms in the series expansion. The low temperature cutoffs in the anharmonic cumulant series are determined fulfilling the constraint of the third law of thermodynamics. The general method here proposed has been applied to the semiclassical Su-Schrieffer-Heeger model whose time dependent source current is linear in the oscillator displacement field. We find that this peculiar current induces large electron-phonon anharmonicities on the phonon subsystem. As a signature of anharmonicity the phonon heat capacity shows a peak whose temperature location strongly varies with the strength of the *e-ph* coupling. Since the electron hopping potential provides a sizeable background in the low and intermediate temperature range, such a peak is partly smeared in the total heat capacity. Low energy oscillators are more sensitive to anharmonic perturbations.

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1 Introduction

There is at present a growing interest in electron-phonon non linearities also triggered by the signatures of a large anharmonicity observed in metal diborides [1]. Phonon anharmonicities have a long story in solid state physics closely related to the inelastic neutron scattering theory [2,3]. As the anharmonic effects are generally small in crystals up to room temperature, second order perturbation theory suffices to determine the lifetime due to three phonons decay processes while the renormalization of the frequencies, together with the three phonons terms, also requires computation of the four phonons vertex in the first order diagram plus a (dominant) contribution due to the thermal expansion of the crystal [4]. It is known [5–7] that most properties of real materials can be well described by replacing the anharmonic phonons with the temperature dependent renormalized harmonic phonons, that is assuming quasi-harmonic vibrational models [8]. Instead, the damping of some anomalous bulk and surface phonons requires explicit computation of the anharmonic interactions [9,10]. However, neither first principles calculations of anharmonicities based on density functional perturbation theory [11] nor empirical force constant approaches do separate the bare phonon-phonon interactions from the non linearities due to the electron-phonon coupling. The latter contribution is generally incorporated in

the former by fitting the third and fourth derivatives of the interatomic potential to experimental thermoelastic properties. In systems such as polymers, whose thermal and conducting behavior is shaped by the strength of the *e-ph* coupling, one would desire to estimate the amount of *e-ph* anharmonicity which may become relevant both in the intermediate and in the low temperature region, in the latter the phonon-phonon interactions tend to vanish.

Theoretical investigations on polymers usually depart from the Su-Schrieffer-Heeger (SSH) Hamiltonian [12–14] in which the *e-ph* coupling is the derivative of the electron hopping integral with respect to the intersite atomic displacement. As the electron propagator couples to the oscillator displacement the SSH model can be attacked by the path integral method [15–17] which allows one to derive the time dependent probability amplitude for a particle in a bath of oscillators. On the other hand, considering the electron particle path as the disturbing source for the phonon subsystem one may evaluate the amount of *e-ph* anharmonicity by expanding perturbatively the phonon partition function. A study of the cumulant terms versus temperature would permit to assess the relevance of the *e-ph* interactions in the SSH model. This paper addresses precisely this issue focusing on the computation of some equilibrium thermodynamical properties of the harmonic oscillators perturbed by the *e-ph* coupling. The path integral method for the model Hamiltonian is outlined in Section 2. The cumulant expansion is presented in Section 3

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together with the analysis of the anharmonic corrections to phonon free energy and heat capacity. Section 4 contains some final remarks.

2 Hamiltonian model

In one dimension the SSH Hamiltonian is:

$$H = \sum_r J_{r,r+1} (f_r^\dagger f_{r+1} + f_{r+1}^\dagger f_r) \\ J_{r,r+1} = -\frac{1}{2} [J + \alpha(u_r - u_{r+1})] \quad (1)$$

where J is the nearest neighbors hopping integral for an undistorted chain, α is the electron-phonon coupling, u_r is the displacement of the atomic group on the r -lattice site along the molecular axis, f_r^\dagger and f_r create and destroy electrons (i.e., π band electrons in polyacetylene) on the r -group. The non-interacting phonon Hamiltonian is given by a set of independent oscillators. Let's apply to the Hamiltonian in equation (1) space-time mapping techniques previously used i.e. in the path integral formulation of the theory of dilute magnetic alloys [18] and in the path integral study of A15 compounds with strong electron-phonon coupling [19]. On general grounds, the method allows one to account for the time-retarded nature of the interactions. Thus (1) transforms into a time dependent Hamiltonian $H(\tau, \tau')$ after introducing $x(\tau)$ and $y(\tau')$ as the electron coordinates at the r and $r+1$ lattice sites, respectively. The spatial e - ph correlations contained in (1) are then mapped onto the time axis by changing: $u_r \rightarrow u(\tau)$ and $u_{r+1} \rightarrow u(\tau')$. Accordingly we get:

$$H(\tau, \tau') = J_{\tau, \tau'} \left(f^\dagger(x(\tau)) f(y(\tau')) + f^\dagger(y(\tau')) f(x(\tau)) \right) \\ J_{\tau, \tau'} = -\frac{1}{2} [J + \alpha(u(\tau) - u(\tau'))]. \quad (2)$$

The ground state of the SSH Hamiltonian is twofold degenerate and, in real space, a soliton connects the two phases with different senses of dimerization. As a localized electronic state is associated to the soliton the SSH model describes in principle both electron hopping between solitons and thermally activated hopping to band states. By mapping onto equation (2) we introduce time dependent electron hops while maintaining the fundamental features of the SSH Hamiltonian. As the hops are not constrained to first neighbors sites along the chain $H(\tau, \tau')$ is more general than the real space Hamiltonian in (1). Equation (2) shows the semiclassical nature of the model in which quantum mechanical degrees of freedom interact with the classical variables $u(\tau)$. After setting $\tau' = 0$, $u(0) \equiv y(0) \equiv 0$, we take the thermal average for the electron operators over the ground state thus obtaining the average energy per lattice site due to electron hopping plus e - ph coupling:

$$\frac{\langle H(\tau) \rangle}{N} = V(x(\tau)) + u(\tau)j(\tau) \\ j(\tau) = -\alpha \left(G[-x(\tau), -\tau] + G[x(\tau), \tau] \right) \quad (3)$$

where $N = L/a$, with L the chain length and a the lattice constant. $V(x(\tau))$ (proportional to J) is the effective term accounting for the τ dependent electronic hopping while $j(\tau)$ is the external source current for the oscillator field, $G[x(\tau), \tau]$ being the electron propagator.

Let's consider a large number N of lattice sites and associate an oscillator field $u_i(\tau)$ (with $i = 1 \dots N$) to each of them. The set of harmonic oscillators represents the dissipative *bath* for the quantum mechanical particle whose coordinate is $x(\tau)$. As the average electron energy (see Eq. (3)) in our time dependent SSH model depends linearly on each of the phonon coordinates we can solve the electron path integral which is formally given by

$$\langle x(\beta) | x(0) \rangle = \prod_{i=1}^N \int Du_i(\tau) \int Dx(\tau) \\ \times \exp \left[- \int_0^\beta d\tau \sum_{i=1}^N \frac{M_i}{2} (u_i^2(\tau) + \omega_i^2 u_i^2(\tau)) \right] \\ \times \exp \left[- \int_0^\beta d\tau \left(\frac{m}{2} \dot{x}^2(\tau) + V(x(\tau)) - \sum_{i=1}^N u_i(\tau) j(\tau) \right) \right] \quad (4)$$

β is the inverse temperature, m is the electron mass and ω_i are the oscillators frequencies. The oscillator masses are considered as independent of i , $M_i \equiv M$ and hereafter we set $M = 10^4 m$.

The oscillators coordinates can be straightforwardly integrated over the paths $Du_i(\tau)$ and after imposing a closure condition ($x(\beta) = x(0)$) on the electron particle paths, we obtain the total partition function in the functional form:

$$Z(j(\tau)) = Z_{ph} \oint Dx(\tau) \exp \left[- \frac{m}{2} \dot{x}^2(\tau) \right. \\ \left. - V(x(\tau)) - A(j(\tau)) \right] \\ Z_{ph} = \prod_{i=1}^N \frac{1}{2 \sinh(\hbar\omega_i\beta/2)} \\ A(j(\tau)) = -\chi \sum_{i=1}^N \frac{1}{\hbar\omega_i \sinh(\hbar\omega_i\beta/2)} \int_0^\beta d\tau G[x(\tau), \tau] \\ \times \int_0^\beta d\tau'' \cosh(\omega_i(|\tau - \tau''| - \beta/2)) \\ \times G[x(\tau''), \tau''] \\ \chi = \frac{\hbar^2 \alpha^2}{4M}. \quad (5)$$

The nonequilibrium quantum statistics of the system can be derived via (4) through the closed-time path formalism [20] which permits to evaluate dissipative properties due to the phonon bath friction [21]. The thermodynamical properties of the full interacting system are

obtained by computing (5) after introducing a measure of integration for the electron paths as detailed in reference [22]. In the present paper we focus on the equilibrium thermodynamics of the phonon bath interacting with the quantum particle of the Hamiltonian model whereas we neglect phonon-phonon interactions whose effects become relevant at high temperatures [23].

3 Electron-phonon anharmonicity

In general, the phonon partition function perturbed by a source current $j(\tau)$ can be expanded in anharmonic series as:

$$Z_{ph}[j(\tau)] \simeq Z_{ph} \left(1 + \sum_{l=1}^k (-1)^l \langle C^l \rangle_{j(\tau)} \right) \quad (6)$$

where the cumulant terms $\langle C^l \rangle_{j(\tau)}$ are expectation values of powers of correlation functions of the perturbing potential. The averages are meant over the ensemble of the harmonic oscillators whose partition function is Z_{ph} .

A) As a first step we consider the general problem of an electron path linearly coupled to a single oscillator with energy ω and displacement $u(\tau)$, through the current $j_x(\tau) = -\alpha x(\tau)$. In this case odd $-k$ cumulant terms vanish and the lowest order even $-k$ cumulants can be derived as shown in the Appendix. To obtain a closed analytical expression for the cumulants to any order we approximate the electron path by its τ averaged value: $\langle x(\tau) \rangle \equiv \frac{1}{\beta} \int_0^\beta d\tau x(\tau) = x_0/a$ and expand the oscillator path in N_F Fourier components:

$$u(\tau) = u_o + \sum_{n=1}^{N_F} 2 \left(\Re u_n \cos(\omega_n \tau) - \Im x_n \sin(\omega_n \tau) \right) \\ \omega_n = 2\pi n / \beta. \quad (7)$$

Next we choose the measure of integration

$$\oint Du(\tau) \equiv \frac{\sqrt{2}}{(2\lambda_M)^{(2N_F+1)}} \int_{-\infty}^{\infty} du_o \\ \times \prod_{n=1}^{N_F} (2\pi n)^2 \int_{-\infty}^{\infty} d\Re u_n \int_{-\infty}^{\infty} d\Im u_n \quad (8)$$

being $\lambda_M = \sqrt{\pi \hbar^2 \beta / M}$. Such a measure normalizes the kinetic term in the oscillator field action

$$\oint Du(\tau) \exp \left[-\frac{M}{2} \int_0^\beta d\tau \dot{u}^2(\tau) \right] \equiv 1. \quad (9)$$

Then, using equations (7, 8) and equation (14) in Appendix, we obtain for the k th cumulant

$$\langle C^k \rangle_{N_F} = Z_{ph}^{-1} \frac{(\alpha_R \beta \lambda_M)^k (k-1)!!}{k! \pi^{k/2} (\omega \beta)^{k+1}} \\ \times \prod_{n=1}^{N_F} \frac{(2n\pi)^2}{(2n\pi)^2 + (\omega \beta)^2} \\ \alpha_R = \alpha x_0 / a \quad (10)$$

Let's set $x_0/a = 0.1$ in the following calculations thus reducing the effective coupling α_R by one order of magnitude with respect to the bare value. However, the trend shown by the results hereafter presented does not depend on this choice since x_0/a and α can be varied independently. As the cumulants should be stable against the number of Fourier components in the oscillator path expansion, using (10) we set the minimum N_F through the condition $2N_F\pi \gg \omega\beta$. The thermodynamics of the anharmonic oscillator can be computed by the cumulant corrections to the harmonic phonon free energy:

$$F^{(k)}(T) = -\frac{1}{\beta} \ln \left[1 + \sum_{l=1}^k \langle C^{2l} \rangle_{N_F} \right]. \quad (11)$$

To proceed one needs a criterion to find the temperature dependent cutoff k^* in the cumulant series. We feel that, in the low T limit, the third law of thermodynamics may offer the suitable constraint to determine k^* . Then, given α and ω , the program searches for the cumulant order such that the heat capacity and the entropy tend to zero in the zero temperature limit. At any finite temperature T , the constant volume heat capacity is computed as

$$C_V^{(k)}(T) = - \left[F^{(k)}(T + 2\Delta) - 2F^{(k)}(T + \Delta) + F^{(k)}(T) \right] \\ \times \left(\frac{1}{\Delta} + \frac{T}{\Delta^2} \right) \quad (12)$$

Δ being the incremental step and k^* is determined as the minimum value for which the heat capacity converges with an accuracy of 10^{-4} . Figures 1a and 1b show phonon heat capacity and free energy respectively in the case of a low energy oscillator for an intermediate value of e - ph coupling. Harmonic functions, anharmonic functions with second order cumulant and anharmonic functions with k^* corrections are reported on in each figure. The second order cumulant is clearly inadequate to account for the low temperature trend yielding a negative phonon heat capacity below ~ 40 K while at high T the second order cumulant contribution tends to vanish. Instead, the inclusion of k^* terms in equations (11, 12) leads to the correct zero temperature limit although there is no visible anharmonic effect on the phonon heat capacity throughout the whole temperature range being $C_V^{(k^*)}$ perfectly superimposed to the harmonic C_V^h . Note in Figure 1b that

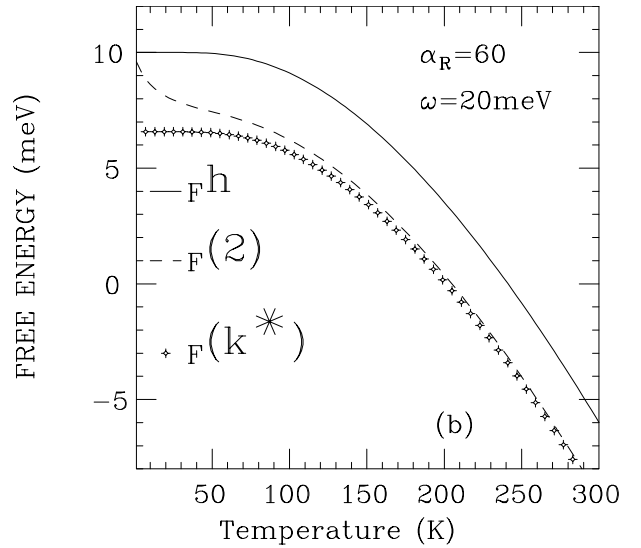
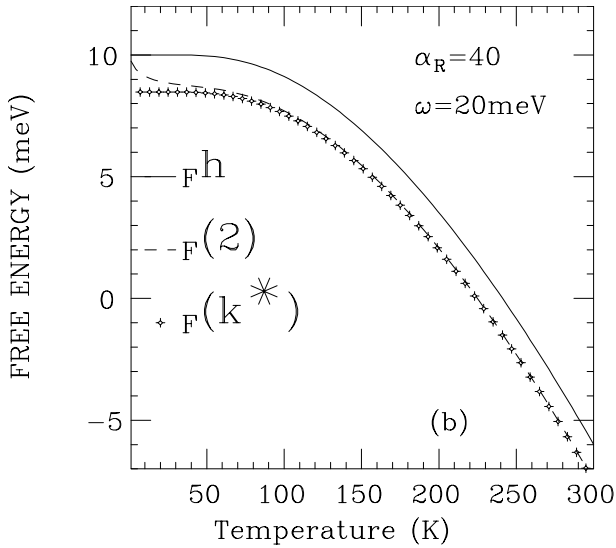
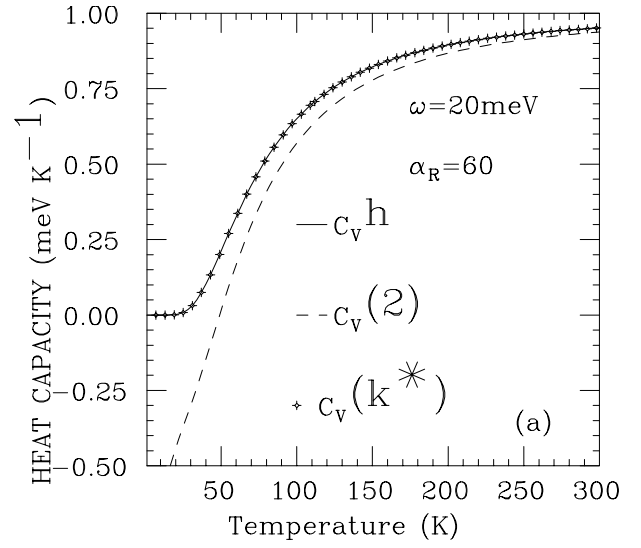
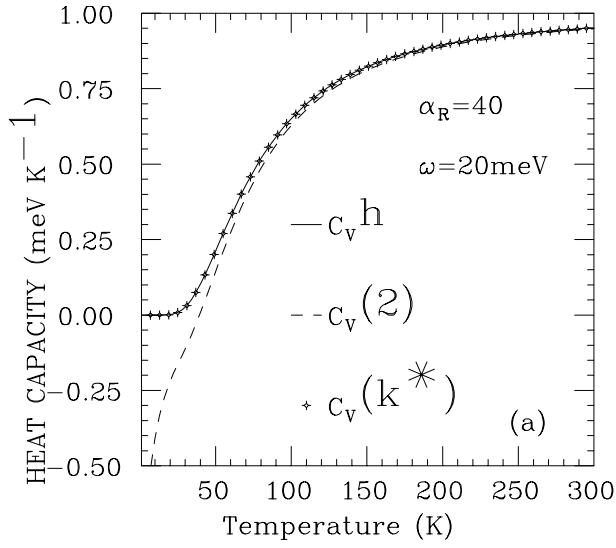


Fig. 1. (a) Phonon heat capacity and (b) Phonon free energy calculated in the harmonic model (solid line), the anharmonic model with second order cumulant (dashed line), anharmonic model with k^* cumulants (symbols). α_R is the effective e - ph coupling in units meV \AA^{-1} and ω is the phonon energy.

Fig. 2. As in Figure 1 but with larger e - ph coupling.

the k^* corrections simply shift downwards the free energy without changing its slope versus temperature. By increasing α_R , the low T range with wrong (negative) $C_V^{(2)}$ broadens (see Fig. 2a) whereas the k^* contributions permit to fulfill the zero temperature constraint and substantially lower the phonon free energy (see Fig. 2b). Thus, for the particular choice of constant (in τ) source current we find that the e - ph anharmonicity renormalizes the phonon partition function although no change occurs in the thermodynamical behavior of the free energy derivatives. Anharmonicity is essential to stabilize the system but it leaves no trace in the heat capacity [24]. Figure 3a displays the k^* temperature dependence for three choices of e - ph coupling in the case of a low energy oscillator: while, at high T , the number of required cumulants ranges between

six and ten according to the coupling, k^* strongly grows at low temperatures getting the value 100 at $T = 1$ K for $\alpha_R = 60 \text{ meV \AA}^{-1}$. The k^* versus α_R behavior is pointed out in Figure 3b for three selected temperatures: at low T the cutoff strongly varies with the strength of the coupling while, by enhancing T , the number of cumulant terms in the series is smaller and becomes much less dependent on α_R . Figure 3c shows that by decreasing the oscillator energy an increasing number of cumulants has to be taken into account to make the thermodynamical functions convergent. At $T = 5$ K the oscillator with $\omega \sim 20 \text{ meV}$ requires ~ 40 cumulant terms to stabilize its thermodynamical properties. Instead, a cutoff $k^* \sim 10$ suffices for $\omega \sim 100 \text{ meV}$ even at low temperatures [25] consistently with the expectations that high energy oscillators are less sensitive to e - ph induced anharmonicity.

B) Next we turn to the computation of the equilibrium thermodynamics of the phonon subsystem perturbed by the source current of the semiclassical SSH model

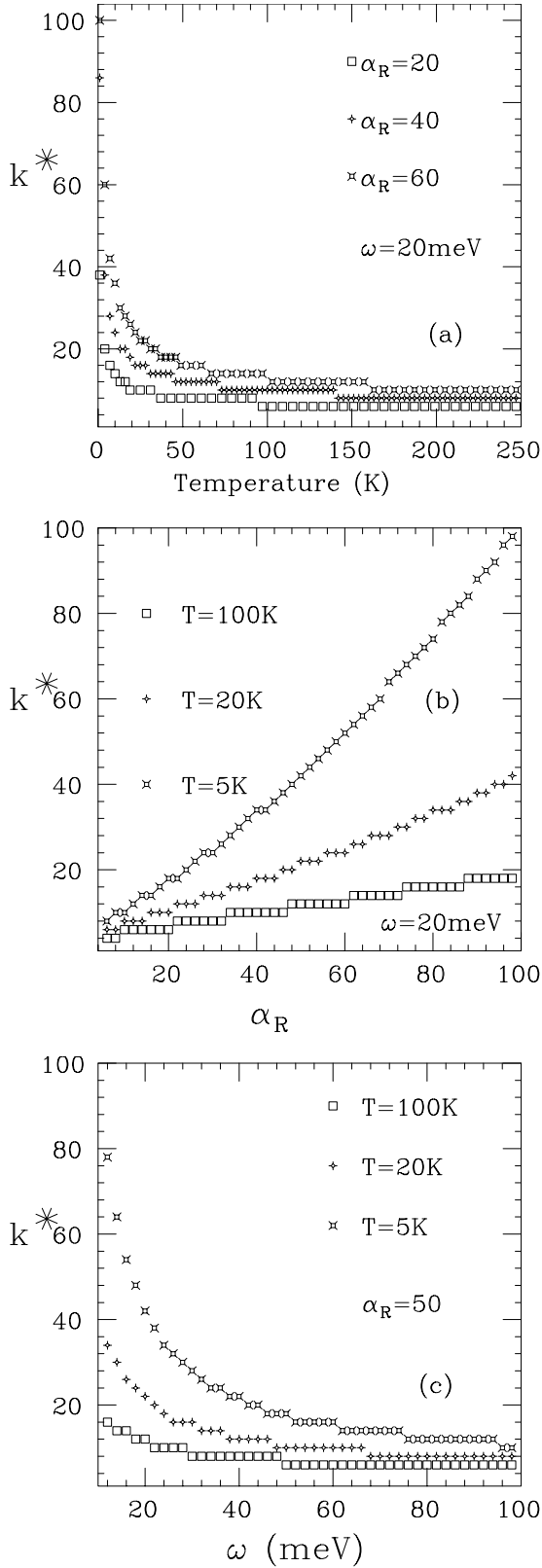


Fig. 3. (a) Cutoff k^* in the cumulant expansion versus temperature for three values of e - ph coupling (in units meV \AA^{-1}). (b) Cutoff k^* in the cumulant expansion versus e - ph coupling for three selected temperatures. (c) Cutoff k^* in the cumulant expansion versus oscillator energy for three selected temperatures.

described in Section 2. Assuming that the electron particle path interacts with each of the N oscillators through the coupling α (taken independent of i), we write the k th cumulant term as

$$\begin{aligned} \langle C^k \rangle_{j(\tau)} = & Z_{ph}^{-1} \prod_{i=1}^N \oint D u_i(\tau) \\ & \times \frac{1}{k!} \prod_{l=1}^k \left[\int_0^\beta d\tau_l u_i(\tau_l) j(\tau_l) \right]^l \\ & \times \exp \left[- \int_0^\beta d\tau \sum_{i=1}^N \frac{M_i}{2} (\dot{u}_i^2(\tau) + \omega_i^2 u_i^2(\tau)) \right] \end{aligned} \quad (13)$$

where $j(\tau)$ is given by equation (3). Since the oscillators are intact decoupled in our model (and anharmonic effects mediated by the electron particle path are neglected) the behavior of the cumulant terms $\langle C^k \rangle_{j(\tau)}$ can be studied by selecting a single oscillator having energy ω and displacement $u(\tau)$.

As the electron propagator depends on the bare hopping integral we set $J = 100$ meV thus assuming a narrow band electron system consistently with our previous studies. Any electron path yields in principle a different cumulant contribution. Numerical investigation shows however that convergent k -order cumulants are achieved by: i) taking $M_F = 2$ Fourier components in the electron path expansion, ii) setting for the coefficients $\{x_o, c_m\}$ a maximum amplitude of order 0.1 (in units of the lattice constant) and iii) summing over $\sim 5^{2M_F+1}$ electron paths.

As in the case A), we truncate the cumulant series by invoking the third law of thermodynamics to determine the cutoff k^* in the low temperature limit and by searching numerical convergence on the first and second free energy derivatives at any finite temperature. k^* does not depend on the specific electron path coefficients then, $\langle C^{k^*} \rangle = \sum_{(x_o, c_m)} \langle C^{k^*} \rangle_{(x_o, c_m)}$. Again, we can start our analysis from (11) after checking that odd k cumulants yield vanishing contributions. Now however the picture of the anharmonic effects changes drastically. The e - ph coupling strongly modifies the shape of the heat capacity and free energy plots with respect to the harmonic result as it is seen in Figures 4a and b respectively. The heat capacity versus temperature curves show a peculiar peak above a threshold value $\alpha \sim 10$ meV \AA^{-1} which clearly varies according to the energy of the harmonic oscillator. Here we set $\omega = 20$ meV to emphasize the size of the anharmonic effects on a low energy oscillator. By enhancing α the height of the peak grows and the bulk of the anharmonic effects on the heat capacity is shifted towards lower T . At $\alpha \sim 60$ meV \AA^{-1} the crossover temperature is around 100 K. Note that the size of the anharmonic enhancement is ~ 10 times the value of the harmonic oscillator heat capacity at $T = 100$ K. However such a large anharmonic effect on the phonon subsystem is partly covered in the total heat capacity by the source action $A(j(\tau))$ and mainly by the hopping potential $V(x(\tau))$ (see Eqs. (5)) contributions analysed in reference [22]. Taken for instance a bath of ten low energy oscillators with $\omega = 20$ meV,

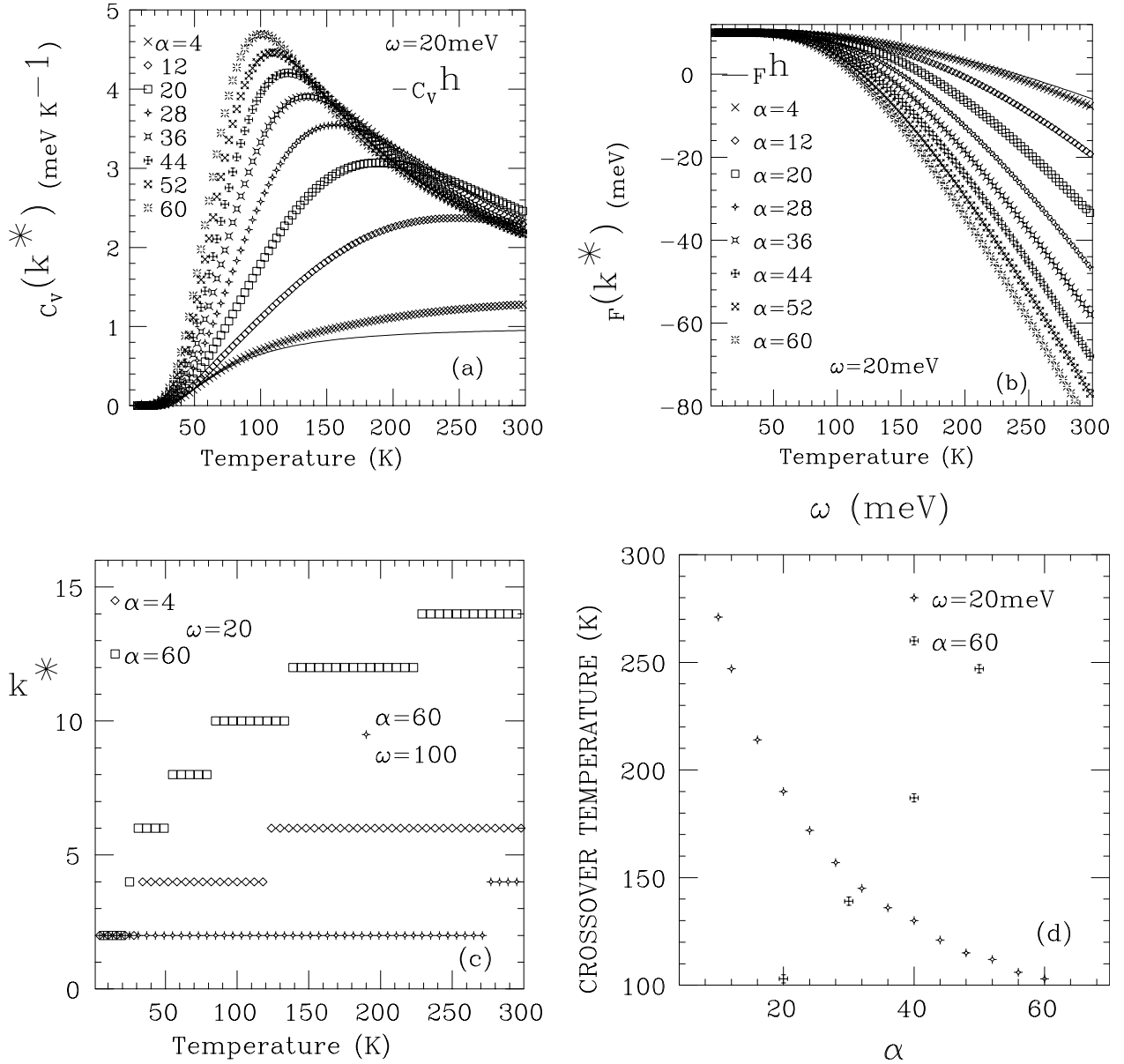


Fig. 4. Anharmonic (a) phonon heat capacity and (b) free energy versus temperature for eight values of e - ph coupling. The harmonic plots are also reported on. A low energy oscillator is assumed. (c) Temperature dependence of the cutoff k^* for: a low energy oscillator ($\omega = 20$ meV) with two values of e - ph couplings; a high energy oscillator ($\omega = 100$ meV) with a strong e - ph coupling value. (d) Temperatures at which the heat capacity shows the peak (see Fig. 4a) versus e - ph coupling at fixed ω (bottom axes) and versus ω at fixed coupling (top axes).

setting $\alpha \sim 60$ meV \AA^{-1} which implies an effective coupling $\chi \sim 700$ meV³ (last of Eqs. (5)) we get a source heat capacity a factor two larger than the harmonic phonon heat capacity at temperatures of order 100 K. Thus the anharmonic peak, although substantially smeared by the electronic contributions to the total heat capacity, should still appear in systems with low energy phonons and sizeable e - ph coupling to which the SSH Hamiltonian applies. It is worth noting that recent numerical studies of a classical one dimensional anharmonic model undergoing a Peierls instability [26] also find a specific heat peak as a signature of anharmonicity.

At high T the anharmonic corrections renormalize downwards the free energy but their effect on the heat capacity tends to decrease signalling that e - ph nonlinearities are rather to be seen in the intermediate to low temperature range.

Also the k^* versus T behavior described in Figure 4c is much different from the previous case (see Fig. 3a): a few cumulant terms suffice at low temperatures even at large e - ph couplings ($\alpha \sim 60$ meV \AA^{-1}) and for a low energy oscillator whereas k^* grows by increasing T both for weak and strong α . Then, $k^*(T)$ does not necessarily provide a measure of the degree of e - ph anharmonicity as revealed

by the heat capacity behavior. At room temperature, we find $k^* = 14$ in the strong coupling case with $\omega = 20$ meV while, by taking $\omega = 100$ meV, k^* drops attaining the value 4. This would suggest that also in the SSH model high energy phonons are expected to be less anharmonic. The latter idea is confirmed by looking at Figure 4d where the crossover temperature in the oscillator heat capacity curves is reported on versus α at fixed $\omega = 20$ meV (lower axes) and versus ω at fixed $\alpha = 60$ meV \AA^{-1} (upper axes) respectively. The following main features may be observed: i) the peak is located at decreasing T by increasing α (as clearly seen also in Fig. 4a); ii) there is no crossover at high energies since the heat capacity has a positive derivative in the whole range of temperatures; iii) by decreasing ω , the peak shows up at $\omega \leq 50$ meV and its temperature location is shifted downwards taking lower oscillator energies. At $\omega = 20$ meV we recover the crossover at $T \simeq 100$ K.

4 Conclusions

We have studied the equilibrium thermodynamics of an electron-phonon system looking in particular at the anharmonic effects produced by the electronic subsystem on the phonon oscillators. The path integral formalism permits to analyse the e - ph non linearities as a function of the source current (peculiar of the Hamiltonian model) which disturbs the harmonic oscillator. The phonon partition function has been expanded in k -order cumulant series and, in the zero temperature limit, we have set the cutoff k^* imposing the constraint given by the third law of thermodynamics. At any finite temperature, k^* ensures convergence in the first and second free energy derivatives. Rather than being a unique measure of e - ph anharmonicity $k^*(T)$ turns out to be a model dependent function whose values may vary considerably according to the physical quantities one decides to sample. As a general trend we find however that, at fixed T and e - ph coupling, higher energy oscillators are more stable and require a lower k^* for the computation of their thermodynamical properties.

We have first considered the case of a source current proportional to the time averaged electron path and analytically derived the cumulant expansion for the phonon partition function. This current induces a slope preserving shift in the phonon free energy versus temperature hence, the heat capacity does not show any correction with respect to the harmonic result in spite of the high number of anharmonic terms which appear in the cumulant series.

Next we have studied the semiclassical, one dimensional Su-Schrieffer-Heeger model, a paradigm in polymer physics, and summed the cumulant contributions due to a significant number of electron and oscillator paths. The cutoff k^* depends both on the phonon energy and on the value of the e - ph coupling. At stronger couplings $k^*(T)$ grows faster versus temperature. Using the time dependent source current proportional to the electron propagator, we find a striking evidence of e - ph anharmonicity in the constant volume heat capacity of a single oscillator. As a main feature the phonon heat capacity exhibits a peak whose height and location on the T axis varies with

the energy of the oscillator and the strength of the e - ph coupling: while high energy phonons prove to be less affected by e - ph corrections, strong couplings shift the main body of the anharmonic effects towards low T . To point out the relevance of the e - ph anharmonicities we have selected a low energy oscillator and, for the largest e - ph coupling value here considered, we have found a broad peak whose maximum is roughly ten times over the harmonic phonon background at $T \sim 100$ K. Such a large effect should be however partly smeared in the total heat capacity as the electron hopping potential of the Su-Schrieffer-Heeger Hamiltonian provides a large contribution both at intermediate and at low temperatures. As seen in a previous investigation [22] the time dependent hopping potential ($V(x(\tau))$ in Eq. (3)) is infact responsible for the characteristic upturn in the *total heat capacity over T* ratio observed *at low T* and indicating that a glassy like behavior can arise in the linear chain.

Thus, the present study is meant as complementary to our cited previous analysis in the sense that here we have found, mainly *at intermediate T* , sizeable electron-phonon anharmonicities in the thermodynamics of low energy oscillators, essentially ascribable to the peculiar time dependent source current ($j(\tau)$ in Eq. (3)) which linearly couples to the oscillator field.

Appendix

Let's assume a source current $j_x(\tau) = -\alpha x(\tau)$ as the disturbing term for a single oscillator field, α being the e - ph coupling, M the atomic mass and $x(\tau)$ the electron path. Then the k th order cumulant term contributing to the $x(\tau)$ - perturbed phonon partition function is given by

$$\langle C^k \rangle_{x(\tau)} = Z_{ph}^{-1} \frac{\alpha^k}{k!} \oint Du(\tau) \prod_{l=1}^k \left[\int_0^\beta d\tau_l u(\tau_l) x(\tau_l) \right]^l \times \exp \left[- \int_0^\beta d\tau \frac{M}{2} (\dot{u}^2(\tau) + \omega^2 u^2(\tau)) \right]. \quad (14)$$

We use the oscillator path and the functional measure of integration given in the equations (7, 8) of the text respectively. Then, the electron path expansion in Fourier components

$$x(\tau) = x_o + \sum_{m=1}^{M_F} \left(c_m \cos(\omega_m \tau) + d_m \sin(\omega_m \tau) \right) \\ \omega_m = 2\pi m / \beta \\ c_m = 2\Re x_m \\ d_m = -2\Im x_m \quad (15)$$

will be truncated at $M_F = N_F$. Without any loss of generality we set $d_m = 0$ and derive the following expressions

for the lowest even order cumulants:

$$\begin{aligned}
\langle C^2 \rangle_{(x_o, c_m)} &= Z_{ph}^{-1} \frac{\alpha^2 (\beta \lambda_M)^2}{2 \beta \omega} F(N_F) \cdot \left[\frac{x_o^2}{\pi (\beta \omega)^2} \right. \\
&\quad \left. + \frac{1}{2\pi} \sum_{m=1}^{N_F} \frac{c_m^2}{(2\pi m)^2 + (\beta \omega)^2} \right] \\
\langle C^4 \rangle_{(x_o, c_m)} &= Z_{ph}^{-1} \frac{\alpha^4 (\beta \lambda_M)^4}{4! \beta \omega} F(N_F) \cdot \left[\frac{3x_o^4}{2\pi^2 (\beta \omega)^4} \right. \\
&\quad + \frac{3x_o^2}{2\pi^2 (\beta \omega)^2} \sum_{m=1}^{N_F} \frac{2c_m^2}{(2\pi m)^2 + (\beta \omega)^2} \\
&\quad + \frac{3}{8\pi^2} \sum_{m=1, l>m}^{N_F} \frac{2c_m^2}{(2\pi m)^2 + (\beta \omega)^2} \\
&\quad \times \frac{2c_l^2}{(2\pi l)^2 + (\beta \omega)^2} \\
&\quad \left. + \frac{3}{4\pi^2} \sum_{m=1}^{N_F} \frac{c_m^4}{((2\pi m)^2 + (\beta \omega)^2)^2} \right] \\
F(N_F) &= \prod_{m=1}^{N_F} \frac{(2\pi m)^2}{(2\pi m)^2 + (\beta \omega)^2}. \tag{16}
\end{aligned}$$

Odd k -cumulants vanish at any order. Setting a maximum amplitude for the coefficients x_o and c_m and integrating equations (16) over a class of electron paths one finds the total cumulant contributions to the partition function.

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