Seebeck coefficient in low-dimensional fluctuating charge density wave systems

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We study the role of charge density wave fluctuations on the temperature dependence of Seebeck coefficient in quasi-one-dimensional conductors with a Peierls instability. The description of low-dimensional incommensurate charge density wave fluctuations as obtained by a generalized Ginzburg-Landau approach for arrays of weakly coupled chains is embodied in the numerical solution of the semiclassical Boltzmann transport equation. The energy and temperature dependence of the scattering time of electrons on fluctuations can then be extracted and its influence on the Seebeck coefficient calculated. The connection between theory and experiments carried out on molecular conductors is presented and critically discussed.

I. INTRODUCTION

In recent years, the understanding of the role played by fluctuations on transport properties has held particular interest in the study of correlated low-dimensional electron systems. This is the case of the considerable attention devoted to the part played by fluctuations in the origin of linear temperature resistivity which is found, for instance, in the metallic phase of many unconventional superconductors near their quantum critical point [1–5].

Although examined with less sustained attention, the thermopower or the Seebeck coefficient (SC) to which this work is devoted is another transport observable known to be influenced by fluctuations. When coupled to electron degrees of freedom, fluctuations can introduce significant corrections to the free electron gas—linear in temperature T—prediction of the SC [6–13]. According to the well known Mott SC formula [14,15], one difficulty with this quantity is that it is influenced by both thermodynamics and effects linked to the energetic of collisions along the Fermi surface [14,16]. Their respective contributions are not easily disentangled and require a precise knowledge of fluctuations involved and how they couple with electrons.

In the framework of a spin-fermion model [6] and variant of it [8], nearly critical two-dimensional antiferromagnetic fluctuations on thermodynamics was shown to lead to a logarithmic or power law enhancement of specific heat. This was in turn shown to introduce similar temperature dependent corrections to the thermodynamic SC component. A logarithmic enhancement was found compatible with experiments in some heavy fermions near a magnetic quantum critical point [17]. As for the influence of the energy and momentum dependence of inelastic scattering time on SC, it has also been analyzed in different correlated systems. In the case of the single band repulsive Hubbard model in two dimensions, for instance, the combination of linearized Boltzmann theory and the renormalization group method has made it possible to calculate the electron-electron Umklapp scattering time,

which contributes distinctly from thermodynamics to the deviations from a linear-T SC [9,10], as they can be found in cuprates and pnictides as a function of doping [18,19]. The same combination of techniques has been used to calculate the impact of enhanced Umklapp scattering by antiferromagnetic fluctuations on the SC of quasi-one-dimensional organic metals near a quantum critical point that connects a spin-density-wave state to superconductivity under pressure [13].

In order to further assess the part played by the collision dynamics in the temperature profile of SC, it would be of primary interest to examine the problem in well characterized electron systems known to be among the simplest ones dominated by quasicritical fluctuations. This is the case of low-dimensional metals undergoing a Peierls instability. It corresponds to the formation of a lattice distortion that is adiabatically connected with a charge density wave (CDW) superstructure. In Peierls systems, the coupling between electrons and low energy CDW fluctuations takes its origin in the electron-phonon interaction, a connection which is well understood. An additional simplification resides in the fact that for many of them the Fermi surface is found to be particularly simple, reducing essentially to a plain—one-dimensional—pointlike structure.

The organic charge transfer salt TTF-TCNQ is a well known example of such Peierls systems characterized by a broad temperature domain of CDW fluctuations [20]. As a signature of their one-dimensional character, these fluctuations emerge well above the temperature scale of true long-range order, which is ultimately triggered by small but finite interchain coupling [21–23]. The temperature dependence of the SC for this compound in various pressure conditions is well documented [24,25] and will be compared to the theoretical results developed below.

For this purpose, we proceed to the numerical integration of the linearized Boltzmann equation fed by collisions of electrons on low energy quasi-1D CDW fluctuations. The 1D features of fluctuations can be calculated accurately by the functional integral method. The energy profile of the

quasiparticles lifetime across the Fermi level can thus be computed and its contribution to the SC obtained as a function of temperature. A connection between theory and experiments in TTF-TCNQ can be qualitatively established, indicating that the influence of CDW fluctuations on the energy dependence of electron scattering can be a determinant factor in the corrections made to the linear temperature dependence of the Seebeck coefficient of quasi-1D Peierls systems.

In Sec. II the properties of low energy fluctuations for the weakly coupled CDW chains problem are reviewed using the functional integral method. In Sec. III the SC is derived in the framework of the linearized Boltzmann theory and in the presence of CDW fluctuations. In Sec. IV the numerical solution of the Boltzmann equation is carried out and the calculated Seebeck coefficient is critically compared with the available data for TTF-TCNQ. We conclude this work in Sec. V.

II. FLUCTUATIONS OF THE PEIERLS INSTABILITY

We consider the following standard minimal Hamiltonian that captures the CDW phase transition for a set of $N_\perp$ weakly coupled chains of length L

$$H = N_\perp \sum_q \hbar\omega_q\left(b_q^\dagger b_q + \tfrac{1}{2}\right) + \sum_{i,k,\sigma} \epsilon_k\, c_{i,k,\sigma}^\dagger c_{i,k,\sigma}$$
$$\times \frac{1}{\sqrt{L}} \sum_{i,k,q,\sigma} g\, c_{i,k+q,\sigma}^\dagger c_{i,k,\sigma}(b_q + b_{-q}^\dagger) + H_\perp. \quad (1)$$

The first term describes free phonons where $\hbar\omega_q$ is the acoustic phonons spectrum of each chain and $b_q^\dagger$ (b_q) is the creation (destruction) operator of phonon of wave vector q along the chains. The second term corresponds to the noninteracting electron part of each chain i where $c_{i,k,\sigma}^\dagger$ ($c_{i,k,\sigma}$) is the creation (destruction) electron operator of wave vector k and spin σ. We shall consider the tight-binding electron spectrum

$$\epsilon_k = -2t_\parallel \cos kd, \quad (2)$$

which is appropriate for the acceptor TCNQ chains of TTF-TCNQ [26]. Here $t_\parallel$ is the longitudinal hopping and d is the lattice constant along the chains ($L = Nd$). The third term corresponds to the interaction between electrons and phonons whose electron-phonon matrix element g will be considered momentum independent for simplicity. In spite of a purely one-dimensional electron structure in the model, the possibility of three-dimensional CDW order can be assured by an interchain part $H_\perp$ for the repulsive electron-electron (back scattering) interaction between nearest-neighbor chains i and j. It can be written in the form

$$H_\perp = g_\perp \sum_{\langle i,j\rangle} \sum_Q O_i(Q)^\dagger O_j(Q), \quad (3)$$

where $g_\perp > 0$. This repulsive term favors antiphase CDW ordering in the directions perpendicular to the chains; it is expressed in terms of the chain CDW operator

$$O_i(Q) = 1/\sqrt{L} \sum_{k>0,\sigma} c_{i,k-2k_F-Q,\sigma}^\dagger c_{i,k,\sigma}.$$

For the partition function $Z = \text{Tr}\, e^{-\beta(H-\mu N)}$, the partial trace over the harmonic phonon degrees of freedom in H generates a retarded effective interaction between electrons. Together with the transverse part $H_\perp$, both terms can be convert as a coupling to auxiliary CDW fields via a Hubbard-Stratonovich transformation [27,28]. By carrying out the remaining trace over electronic degrees of freedom, the partition function can be put in the following functional integral form

$$Z \rightarrow \iint [\mathfrak{D}\Delta^*\mathfrak{D}\Delta]e^{-\mathcal{H}[\Delta^*,\Delta]}, \quad (4)$$

where $\mathcal{H}[\Delta^*,\Delta]$ is the Landau-Ginzburg Wilson free energy density functional of the CDW field $\Delta^{(*)}$. Up to quartic order at low (Matsubara) frequency $\omega_m = 2\pi m k_B T/\hbar$, small wave vector deviations Q from $2k_F$, and weak interchain coupling $g_\perp$, the functional can be written in the form

$$\mathcal{H}[\Delta^*,\Delta]$$
$$= \sum_{i,\bar{Q}} N(\epsilon_F)\left[\ln T/T_c^0 + \xi_0^2 Q^2 + \Gamma_0|\omega_m|\right]|\Delta_i(\bar{Q})|^2$$
$$+ \frac{k_B T}{L}b\sum_{i,\{\bar{Q}\}} \Delta_i^*(\bar{Q}_1)\Delta_i^*(\bar{Q}_2)\Delta_i(\bar{Q}_3)\Delta_i(\bar{Q}_4)\delta_{\bar{Q}_{1+2}=\bar{Q}_{3+4}}$$
$$+ v_\perp \sum_{\langle i,j\rangle}\sum_{\bar{Q}} \Delta_i^*(\bar{Q})\Delta_j(\bar{Q}) \quad (5)$$
$$\equiv \mathcal{H}_\parallel[\Delta^*,\Delta] + \mathcal{H}_\perp[\Delta^*,\Delta]. \quad (6)$$

The first two terms of (5) define $\mathcal{H}_\parallel$, the intrachain part of the functional, whereas the last term describing the interchain Coulomb interaction between CDW corresponds to the transverse contribution $\mathcal{H}_\perp$. The functional parameters are given by

$$T_c^0 = 1.13\epsilon_F\, e^{-1/\lambda} \quad (\lambda = 2|\bar{g}|^2/\hbar\omega_{2k_F}), \quad (7)$$

$$\xi_0 = \sqrt{\frac{7\zeta(3)}{16}}\frac{\hbar v_F}{\pi k_B T_c^0}, \quad (8)$$

$$\Gamma_0 = \frac{\pi\hbar}{8k_B T_c^0}, \quad (9)$$

$$b = \frac{7\zeta(3)}{16\pi^2}\frac{N(\epsilon_F)}{(k_B T_c^0)^2}, \quad (10)$$

$$v_\perp = N(\epsilon_F)\frac{\bar{g}_\perp}{\lambda^2}, \quad (11)$$

which in order stand for the mean field transition temperature T_c^0, which fixes the scale of fluctuations of isolated chains, the coherence length ξ_0 of $2k_F$ electron-hole pairs, the damping constant Γ_0 of short-range CDW fluctuations, the mode-mode coupling constant b, and finally the reduced interchain coupling $v_\perp$, expressed as a ratio between interchain and intrachain couplings. Here $\bar{Q} = (Q,\omega_m)$, $|\bar{g}|^2 = |g|^2 N(\epsilon_F)$ and $\bar{g}_\perp = g_\perp N(\epsilon_F)$, $N(\epsilon_F) = (\hbar\pi v_F)^{-1}$ being the density of states at the Fermi level with the Fermi velocity $v_F = \frac{1}{\hbar}\nabla_k\epsilon_k|_{k_F}$.

Since $v_\perp$ is small, a perturbative RPA summation for the quasi-1D dynamic CDW susceptibility after analytic continuation to real frequency ($i\omega_m \rightarrow \omega$) leads to:

$$G(Q+2k_F, \boldsymbol{Q}_\perp + \boldsymbol{q}_{\perp 0}, \omega) = \langle \Delta^*(Q,\boldsymbol{Q}_\perp,\omega)\Delta(Q,\boldsymbol{Q}_\perp,\omega)\rangle$$
$$= \frac{G_\parallel(Q+2k_F,\omega)}{1+v_\perp(\boldsymbol{Q}_\perp)G_\parallel(Q+2k_F,\omega)}, \quad (12)$$

where

$$v_\perp(\boldsymbol{Q}_\perp) = -2v_\perp(\cos Q_{\perp y} d_\perp + \cos Q_{\perp z} d_\perp) \quad (13)$$

is the Fourier transform of interchain coupling with the wave vector $\boldsymbol{Q}_\perp = (Q_{\perp y}, Q_{\perp z})$ as deviations with respect to the transverse staggered CDW ordering at $\boldsymbol{q}_{\perp 0} = (\pi/d_\perp, \pi/d_\perp)$, and

$$G_\parallel(Q + 2k_F, \omega) = \langle \Delta^*(Q, \omega)\Delta(Q, \omega)\rangle_\parallel$$

is the 1D dynamic CDW susceptibility. We observe that in the static limit, the RPA summation is equivalent to a molecular field approximation of interchain coupling [29].

To proceed to the evaluation of $G_\parallel$, we first consider the static part

$$G_\parallel(Q + 2k_F, \omega = 0) = \frac{1}{k_B T}\int \langle \Delta^*(x)\Delta(0)\rangle_\parallel \, e^{-iQx} dx, \quad (14)$$

which involves the 1D spatial CDW correlation function

$$\langle \Delta^*(x)\Delta(0)\rangle_\parallel = \frac{1}{Z_\parallel}\iint[\mathfrak{D}\Delta^*\mathfrak{D}\Delta]\,\Delta^*(x)\Delta(0)\,e^{-\beta\mathcal{F}_\parallel[\Delta^*,\Delta]}$$

$$(15)$$

of a complex CDW order parameter $\Delta(x) = |\Delta(x)|e^{i\varphi(x)}$ with amplitude and phase degrees of freedom. In the static limit for $\mathcal{H}_\parallel$ in (6), this correlator is calculated using the static Landau-Ginzburg free energy functional

$$\mathcal{F}_\parallel[\Delta^*, \Delta] = \int_0^L dx\left[a(T)|\Delta(x)|^2 + c\left|\frac{d\Delta}{dx}\right|^2 + b|\Delta(x)|^4\right]. \quad (16)$$

The parameters of the functional are $a(T) = a'\ln T/T_c^0 \simeq a'(T - T_c^0)/T_c^0$, $a' = N(\epsilon_F)$, $c = N(\epsilon_F)\xi_0^2$, and b is given by (10). The statistical mechanics of the CDW Ginzburg-Landau functional can be done accurately by the transfer matrix method [30,31] with the result

$$\langle \Delta^*(x)\Delta(0)\rangle_\parallel = (k_B T_c^0)^2\langle|\bar{\Delta}|^2\rangle_\parallel\, e^{-x/\xi_\parallel}, \quad (17)$$

where $\langle|\bar{\Delta}|^2\rangle_\parallel$ is the mean square of CDW amplitude in the ground state of the transfer matrix Hamiltonian describing a particle moving in the temperature dependent anharmonic Ginzburg-Landau potential well of (16). Here $\bar{\Delta} = \Delta/k_B T_c^0$ is the normalized CDW order parameter. The CDW static correlations with respect to the wave vector $2k_F$ decay exponentially as a function of distance with the characteristic length scale $\xi_\parallel$, corresponding to the 1D CDW correlation length. The transfer matrix results for $\langle|\bar{\Delta}|^2\rangle_\parallel$ and $\xi_\parallel$ for the present Peierls problem are summarized in Fig. 1. The correlation length $\xi_\parallel$ first grows like $(T - T_c^{0*})^{-1/2}$ for temperature $T < 2T_c^0$ down to a seeming ordering scale $T_c^{0*} \sim T_c^0/5$. This scale stands as an effective mean-field temperature that is renormalized downward by amplitude and phase CDW fluctuations. The singularity, however, is preempted from occurring by gapped amplitude modes and dominant gapless phase fluctuations. At $T < T_c^{0*}$, these introduce a crossover toward a $\xi_\parallel \sim 1/T$ singularity, a characteristic of the absence of CDW long-range order at finite temperature in one dimension. As for the temperature dependence of $\langle|\bar{\Delta}|^2\rangle_\parallel$ displayed in Fig. 1,
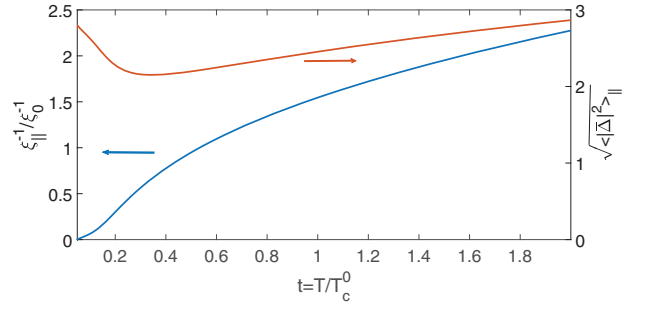

FIG. 1. The results of the transfer matrix method for the temperature dependence of the inverse of CDW correlation length (left scale) and the mean square fluctuations of the normalized order parameter in the ground state of the transfer matrix Hamiltonian (right scale).

it is finite at all temperatures and shows a regular drop down to $T \sim T_c^{0*}$, to finally rise at lower temperature in order to reach the saturation mean-field (Landau) value $(k_B T_c^0)^2\langle|\bar{\Delta}|^2\rangle_\parallel \sim a'/2b$ at zero temperature.

The Fourier transform of (17) leads to the static 1D susceptibility (14), which can be written in the form

$$G_\parallel(Q + 2k_F, 0) = 2k_B T_c^0 \frac{\langle|\bar{\Delta}|^2\rangle_\parallel}{t}\frac{\frac{\xi_0^2}{\xi_\parallel}}{\frac{\xi_0^2}{\xi_\parallel^2} + \xi_0^2 Q^2}, \quad (18)$$

where $t = T/T_c^0$ is the reduced temperature. Above the renormalized mean-field temperature T_c^{0*}, the static 1D susceptibility $G_\parallel(2k_F)$ follows the behavior of $\xi_\parallel \sim (T - T_c^{0*})^{-1/2}$. This is followed by a crossover toward a $G_\parallel(2k_F) \sim T^{-2}$ temperature dependence below T_c^{0*}, a zero temperature singularity characteristic of gapless low energy phase modes whose frequency varies linearly with the wave vector [32].

The denominator of the expression (18) shows the same Q development initially obtained for the quadratic part of the 1D functional $\mathcal{H}_\parallel$ in (5). So, this suggests that a generalization leading to the frequency dependent expression $G_\parallel(Q + 2k_F, \omega)$ can be obtained by simply adding the damping term $-i\Gamma_0\omega$ to the denominator of (18), with the result

$$G_\parallel(Q + 2k_F, \omega) = 2k_B T_c^0\frac{\langle|\bar{\Delta}|^2\rangle_\parallel}{t}\frac{\xi_\parallel}{1 + \xi_\parallel^2 Q^2 - i\Gamma_\parallel\omega}, \quad (19)$$

where the $\Gamma_\parallel = \Gamma_0\xi_0^2/\xi_\parallel^2$ is the damping constant for CDW correlations of size $\xi_\parallel$.

III. LINEARIZED BOLTZMANN APPROACH TO THE SEEBECK COEFFICIENT

We approach the problem of scattering of one-dimensional carriers of charge e on quasi-1D CDW fluctuations in terms of the Boltzmann equation. In the presence of the electric field $\mathcal{E}$ set up by the thermal gradient $\nabla_x T$ parallel to chains, the stationary form of the transport equation for the Fermi distribution f_k reads

$$\left[\frac{\partial f_k}{\partial t}\right]_{\text{coll}} = e\mathcal{E}\,\nabla_{\hbar k}f_k - \frac{(\epsilon_k - \mu)}{T}\nabla_x T\,\nabla_{\hbar k}f_k, \quad (20)$$

where e is the electron charge and μ is the chemical potential.

We seek a solution for $f_k \simeq f_k^0 + f_k^0[1 - f_k^0]\phi_k$ that is linear in the deviations ϕ_k from the free equilibrium distribution $f_k^0 = (e^{\beta(\epsilon_k - \mu)} + 1)^{-1}$. For the collision term we shall consider exclusively the inelastic scattering of electrons on low energy charge CDW fluctuations near $2k_F$. The much weaker contribution of regular scattering of electrons on impurities and defects on both the amplitude of the scattering time and its energy profile can be safely ignored [33].

In this scheme, the Fermi golden rule for the collision term for CDW on the left hand side of (20) can be written in the linear form

$$
\left[\frac{\partial \phi_k}{\partial t}\right]_{\text{coll}} = -\frac{2}{\hbar} |g|^2 \sum_{k'} \frac{1 - f_{k'}^0}{1 - f_k^0} (1 - \delta_{kk'}) \phi_{k'}
$$
$$
\times \int_{-\infty}^{+\infty} n(\omega) \Im m \chi(k' - k, \omega) \delta(\epsilon_{k'} - \epsilon_k - \hbar\omega),
\tag{21}
$$

where $n(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}$ is the Bose factor and $\Im m \chi(k' - k, \omega)$ is the imaginary part of the retarded phonon Green function. The latter can be connected to the CDW retarded

response by replacing the phonon operators by their CDW macroscopic configurations, namely $b^{(\dagger)} \to \Delta^{(*)}/(2g)$. Thus from the fluctuation-dissipation theorem, the imaginary part of intrachain CDW response can be related to the strength of fluctuations obtained from (12). At low frequency, one finds

$$
\Im m \chi(Q + 2k_F, \omega) = \frac{\beta\hbar\omega}{2|g|^2}
$$
$$
\times \frac{1}{N_\perp^2} \sum_{\mathbf{Q}_\perp} \Re e \, G(Q + 2k_F, \mathbf{Q}_\perp + \mathbf{q}_\perp^0, \omega),
\tag{22}
$$

which is strongly peaked at $\hbar\omega \sim \epsilon_{k'} - \epsilon_k$. Performing the frequency integration in (21), the linearized Boltzmann equation can be written in the following integral form

$$
\left[\frac{\partial \phi_k}{\partial t}\right]_{\text{coll}} = k_B \beta^2 v_k(\epsilon_k - \mu)\nabla_x T - e\beta\mathcal{E}v_k
$$
$$
= -\mathcal{L}\phi_k = -\sum_{k'} \mathcal{L}_{kk'}\phi_{k'},
\tag{23}
$$

from which we define the collision operator

$$
\mathcal{L}_{kk'} = \frac{2}{t^2} \frac{1}{LN_\perp^2} \sum_{k',\mathbf{Q}_\perp} \frac{1 - f_{k'}^0}{1 - f_k^0} \hbar^{-1}(\epsilon_{k'} - \epsilon_k) n[(\epsilon_{k'} - \epsilon_k)/\hbar] \langle |\bar{\Delta}|^2 \rangle_\parallel \xi_\parallel
$$
$$
\times \left(\frac{1 + \xi_\parallel^2(k' - k)^2 - Y_\perp(\mathbf{Q}_\perp)}{[1 + \xi_\parallel^2(k' - k)^2 - Y_\perp(\mathbf{Q}_\perp)]^2 + (\Gamma_\parallel/\hbar^2)(\epsilon_{k'} - \epsilon_k)^2}\right)(1 - \delta_{kk'}).
\tag{24}
$$

The transverse part is given by

$$
Y_\perp(\mathbf{Q}_\perp) = \frac{4\alpha}{t} \langle |\bar{\Delta}|^2 \rangle_\parallel \frac{\bar{g}_\perp \xi_\parallel}{\lambda^2 \xi_0} (\cos(Q_{\perp y} d_\perp) + \cos(Q_{\perp y} d_\perp))
\tag{25}
$$

and $\alpha \simeq 2.9$.

It is convenient to write the solution for ϕ_k as the sum of two terms

$$
\phi_k = -\mathcal{L}^{-1} k_B \beta^2 v_k(\epsilon_k - \mu)\nabla_x T + \mathcal{L}^{-1} e\beta\mathcal{E}v_k
$$
$$
\equiv -\phi_k^T + \phi_k^\mathcal{E}
\tag{26}
$$

where $\mathcal{L}^{-1}$ is the inverse of the collision operator. The parameters entering in the collision operator are those of the spectrum in (2); together with the scale T_c^0, these fix the Ginzburg-Landau parameters (7)–(10) for 1D fluctuations leading to $\xi_\parallel$ and $\langle |\bar{\Delta}|^2 \rangle_\parallel$. The small interchain coupling (11) in (25) is fixed in order to get the desired true $T_c \ll T_c^0$.

Seebeck coefficient

To obtain the expression for the Seebeck coefficient, we start from the relation of the 1D electric current density along the chains, which to linear order in ϕ reads

$$
j_\parallel = \frac{2e}{L} \sum_k v_k f_k \simeq \frac{2e}{L} \sum_k v_k f_k^0 (1 - f_k^0)(\phi_k^\mathcal{E} - \phi_k^T).
\tag{27}
$$

Using the normalized quantities

$$
\bar{\phi}_k^T = \frac{\phi_k^T}{k_B \beta^2 v_k(\epsilon_k - \mu)\nabla_x T}
$$

and

$$
\bar{\phi}_k^\mathcal{E} = \frac{\phi_k^\mathcal{E}}{e\beta v_k \mathcal{E}}.
$$

The longitudinal current density can then be written in the form

$$
j_\parallel = K_{11}\mathcal{E} - K_{12}\nabla_x T.
\tag{28}
$$

For open circuit conditions, $j_\parallel = 0$, and the expression for the SC follows,

$$
Q = \frac{\mathcal{E}}{\nabla_x T} = \frac{K_{12}}{K_{11}}
$$
$$
= \frac{2eL^{-1} \sum_k k_B \beta^2 v_k^2(\epsilon_k - \mu) f_k^0 (1 - f_k^0)\bar{\phi}_k}{2e^2 L^{-1} \sum_k \beta v_k^2 f_k^0 (1 - f_k^0)\bar{\phi}_k},
\tag{29}
$$

where $\bar{\phi}^{\mathcal{E},T} (\equiv \bar{\phi}_k)$ obeys the single equation

$$
\mathcal{L}\bar{\phi}_k = \sum_{k'} \mathcal{L}_{kk'}\bar{\phi}_{k'} = 1,
\tag{30}
$$

whose solutions can be considered as the scattering time of carriers as a function of k or the energy ϵ_k. Since at low temperature the product of Fermi distribution factors in

(29) is strongly peaked at the Fermi level μ, a Sommerfeld development leads to the Boltzmann type of expression

$$Q = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left[\frac{d \ln N(\epsilon_k)}{d\epsilon_k}\bigg|_\mu + 2 \frac{d \ln v_k}{d\epsilon_k}\bigg|_\mu + \frac{d \ln \bar{\phi}_k}{d\epsilon_k}\bigg|_\mu \right]$$

$$= Q_0 + Q_c. \tag{31}$$

Here Q_0 stands as the band or thermodynamic contribution to the SC, which corresponds to the sum of the first two terms of (31). From the form of spectrum in (2), one recovers the known result

$$Q_0 = -\frac{\pi^2}{3} \frac{k_B}{|e|} \frac{\epsilon_F}{4t_\parallel^2 - \epsilon_F^2} k_B T \tag{32}$$

for the tight-binding electrons in one dimension, where $\epsilon_F = |\epsilon_{k_F}|$.

The last term Q_c is linked to the dynamics of collisions at the Fermi level; it is computed from the numerical solution of (30) using the expression (24) for the collision operator [34]. This will lead to the energy or momentum profile of the collision time across the Fermi level.

IV. NUMERICAL RESULTS

A. One dimension

It is instructive to first consider the results of the above equations for the Seebeck coefficient in the purely 1D limit where $Y_\perp = 0$, namely when the interchain Coulomb term $g_\perp$ is put to zero. The parameters used in the calculations are those typically found for the TCNQ chains of TTF-TCNQ in normal pressure conditions [20,22,26], namely $\rho = 0.59$ for the incommensurate electron concentration taken at low temperature, $t_\parallel = 0.11$ eV for the hopping along the chains and a set of T_c^0 for the scale of 1D CDW fluctuations. The temperature interval for all calculations is fixed to $t \leqslant 2$, namely where $\xi_\parallel \geqslant \xi_0$ and short-range CDW order can be considered as relevant.

In Fig. 2 we show the $k > 0$ dependence of the collision time $\bar{\phi}_k$ near the Fermi point $k_F(t)$ for different reduced temperatures t. The small variation of $k_F(t)$ with temperature is taken into account from the corresponding shift of the chemical potential $\mu(t)$, which is linked by the relation, $\rho = 2/N \sum_k f_k^0$, between the electron concentration ρ and the fermi distribution factor. From the figure, we observe at all t the existence of a minimum in the collision time close to $k_F(t)$, indicating enhanced scattering by CDW fluctuations between k and $k - 2k_F$ states. The minimum deepens as t decreases and fluctuations effects increase. However, the true minimum of $\bar{\phi}_k$ is slightly shifted downward from $k_F(t)$, which reflects the electron-hole asymmetry normally expected for electron carriers for which the collision time increases with energy. This asymmetry introduces a finite positive slope of $\partial \bar{\phi}_k / \partial k|_{k_F(t)}$ ($\equiv \hbar v_k \partial \bar{\phi}_k / \partial \epsilon_k|_{\mu(t)}$), which according to (31) will yield corrections to the linear-T prediction Q_0 for the SC.

The resulting temperature profile of the 1D SC (31) is shown in Fig. 3 for different scales of T_c^0. We observe that in all cases a sublinear temperature dependence in the high temperature domain where amplitude fluctuations are important; it becomes more pronounced with the size of T_c^0. A change of regime is found below $t \sim 1$, where phase fluctuations of the
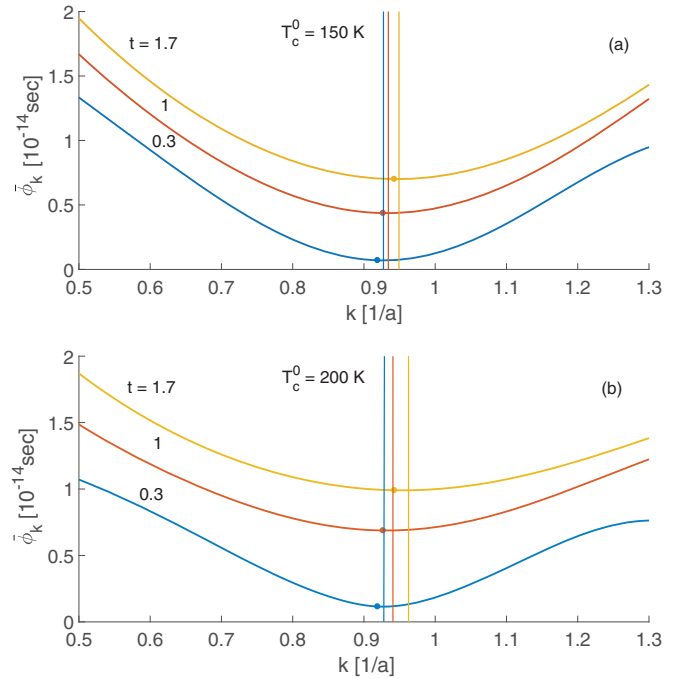

FIG. 2. Collision time as a function of the wave vector k in the neighborhood of the Fermi point $k_F(t)$ at different reduced temperatures $t = T/T_c^0$ in (a) the one-dimensional case for $T_c^0 = 150$ K and (b) for coupled chains at $T_c^0 = 200$ K. The location of $k_F(t)$ as a function of temperature is indicated by vertical lines and the minimum by points.

CDW order parameter emerge; it evolves toward an effective but enhanced T-linear behavior that follows the empirical form [16]

$$Q \approx Q_0(1 + \zeta) \tag{33}$$

with the constant $\zeta > 0$ that increases the slope of Q with T_c^0. Following Refs. [14,16], this is compatible with a power law dependence $\bar{\phi}_k \sim |\epsilon_k|^{-\zeta}$ of the collision time upon the tight-binding energy, which increases as ϵ_k grows (or v_k increases). At very low temperature where $t \ll 1$, $\xi_\parallel$ and phase correlations become very large which deepen the minimum in $\bar{\phi}_k$, resulting in an upturn of the SC.
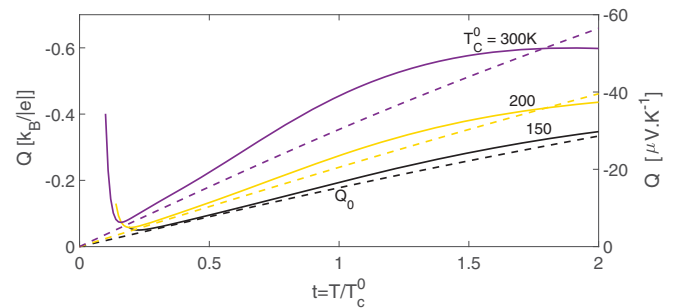

FIG. 3. Calculated one-dimensional Seebeck coefficient as a function of the reduced temperature $t = T/T_c^0$ for different fluctuation scales T_c^0. The dashed lines correspond to the free electron, tight-binding, band contribution Q_0.
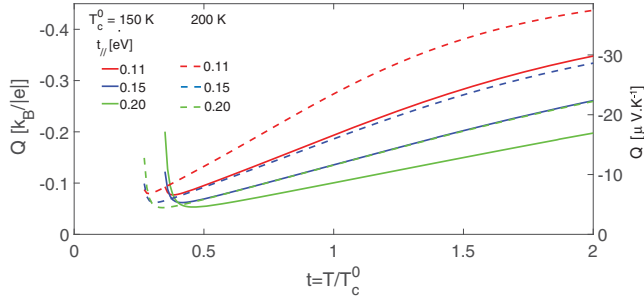
FIG. 4. Calculated three-dimensional Seebeck coefficient as a function of the reduced temperature $t = T/T_c^0$ for different fluctuation scales T_c^0 and band parameters $t_\parallel$.
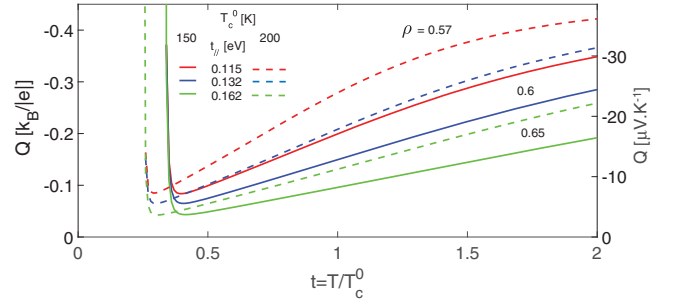

FIG. 5. Calculated three-dimensional Seebeck coefficient as a function of the reduced temperature $t = T/T_c^0$ for different electron concentrations ρ, band parameters $t_\parallel$, and scales T_c^0 for fluctuations.

B. Quasi one-dimensional case

We now turn to the situation where the interchain coupling $g_\perp$ is finite and long-range CDW ordering emerges at $T_c \ll T_c^0$. According to the RPA expression (12), when evaluated at $\boldsymbol{q}_0 = (2k_F, \pi/d_\perp, \pi/d_\perp)$, $g_\perp$ can be fixed in order to give a singularity at $t_c = T_c/T_c^0 \simeq 0.36$ (0.27) for $T_c^0 = 150$ K (200 K) and $t_\parallel = 0.11$ eV, which corresponds to the $T_c \simeq 54$ K typically found for TCNQ chains, using the known low temperature incommensurate electron concentration $\rho = 0.59$ in normal pressure conditions [20]. With these sets of parameters, the variation of the collision time as a function of k across the Fermi point $k_F(t)$ is shown in Fig. 2(b) at different temperatures above t_c for $T_c^0 = 200$ K. From the figure, we observe that for temperatures not too close to t_c, the $\bar{\phi}_k$ and positive slopes at $k_F(t)$ essentially coincide with those found in the 1D case for the same T_c^0, indicating that in this temperature domain the influence of interchain coupling is weak and collisions are primarily governed by 1D fluctuations. As for the dependence on the temperature scale for fluctuations, there is an overall downward shift of $\bar{\phi}_k$ with T_c^0 and an increase in slope at $k_F(t)$.

The temperature dependence of the SC is shown in Fig. 4 for different T_c^0 and band parameters $t_\parallel$. At $t_\parallel = 0.11$ eV, we verify that for both values of T_c^0, the Q temperature dependencies for coupled chains display a sublinear variation that increases with T_c^0 above $t \sim 1$ and an enhanced linear-T behavior below. Both features essentially coincide with those found in Fig. 3 for the 1D case, and this over a large part of the temperature interval. It is only at the approach of t_c where CDW correlations are singular that an upturn in the absolute value of SC is found.

Also shown in the figure is the influence of an increase of the band parameter $t_\parallel$. We observe that as $t_\parallel$ grows, all the above features for Q soften. According to (32), an increase in the electron bandwidth will decrease the slope of Q_0, as normally expected; it will also reduce the collision term Q_c in (31) through an increase of the Fermi velocity or equivalently a decrease in the density of states at the Fermi level.

We close the section by examining the combined influence of varying both $t_\parallel$ and the electron concentration ρ following the relation $\delta \ln \rho \simeq 0.36 \, \delta \ln t_\parallel$, which correlates the average variations of electron concentration ($\delta \ln \rho/\delta P \simeq 0.9\%$/kbar) and hopping ($\delta \ln t_\parallel/\delta P \simeq 2.5\%$/kbar) found in a compressible system like TTF-TCNQ, namely when pressure is applied

and temperature is lowered [20]. This is displayed in Fig. 5 for different T_c^0 compatible with x-ray data [21–23]. Thus an increase of electron concentration ρ in the electron carrier sector $\rho < 1$ for the spectrum (2) produces a decrease of the SC, which adds to that of $t_\parallel$ shown previously in Fig. 4. As ρ grows from its initial average value of 0.57 at ambient pressure, the Fermi point k_F is shifted upward and with it the size of the Fermi velocity. The resulting decrease of the density of states at the Fermi level weakens both Q_0 and Q_c contributions. Thus as ρ and $t_\parallel$ grow, the sublinear T dependence of the Seebeck coefficient is then gradually suppressed; it is replaced by a linear temperature variation with a reduced slope congruent with the empirical expression (33), but with a small ζ. This indicates that at sufficiently large ρ and $t_\parallel$ corrections coming from the collision term become relatively small. This holds outside the critical domain of the transition where fluctuations become large and produce an upturn in $|Q|$ which is more pronounced with increasing ρ (see also Ref. [35]).

V. CONNECTION WITH EXPERIMENTS IN TTF-TCNQ

We now compare the above theoretical results to existing experimental data for the SC in TTF-TCNQ. Although this two-chain charge transfer salt has both electron- and holelike type of carriers pertaining to TCNQ and TTF chains, respectively, the conductivity of TCNQ chains (σ_{TCNQ}) is known to largely dominate that of TTF (σ_{TTF}) [20,25]. Following the expression of the Seebeck coefficient for two type of carriers,

$$Q = \frac{Q_{\mathrm{TCNQ}}\sigma_{\mathrm{TCNQ}} + Q_{\mathrm{TTF}}\sigma_{\mathrm{TTF}}}{\sigma_{\mathrm{TCNQ}} + \sigma_{\mathrm{TTF}}},$$

as weighted by the respective conductivities of the chains. Since $\sigma_{\mathrm{TCNQ}} \gg \sigma_{\mathrm{TTF}}$ holds [25], it will be assumed to be so for the SC, namely that $Q \approx Q_{\mathrm{TCNQ}}$ in the whole temperature range $T_c < T < 2T_c^0$ considered in the present calculations.

We reproduce in Fig. 6 the SC temperature dependence in the chain direction for TTF-TCNQ, as obtained by Chaikin *et al.* [24] at ambient pressure (black dots, $P = 1$bar) and for temperature down to T_c. We first see that the range of $-30\mu \cdot$ V/K reached by the observed Q at ambient temperature is congruent with the one found at $t \sim 2$ in the calculations of Figs. 4 and 5 using the $t_\parallel = 0.11$ eV and the interval of electron concentration $\rho = 0.57–0.59$ and the x-ray scale $T_c^0 = 150–200$ K for the TCNQ chains at ambient pressure [21–23]. Considering the size of the band contribution Q_0
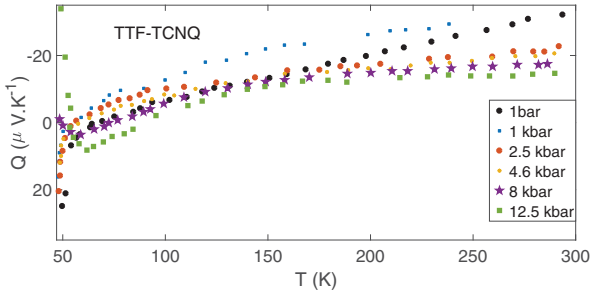
FIG. 6. Seebeck coefficient data as a function of temperature in TTF-TCNQ at ambient and different applied pressures. The data are reproduced down to the close proximity of T_c for the TCNQ chains. After Refs. [24,25].

in Fig. 3, this is compatible with relatively small but finite corrections coming from the collision term. The data show a change of behavior for $T \sim 150$ K below which a more rapid decrease of Q is observed. The progressive increase in the slope of Q as temperature is lowered is however more pronounced than found in the calculations of Figs. 3–5 at $t <$ 1. Experiments rather reveal that Q evolves toward a change of sign as T_c is approached from above, whereas calculations show an enhanced linear-T behavior before an upturn in $|Q|$ at the approach of t_c. The difference may take its origin in a shift of the position of the Fermi level as temperature is lowered and fluctuations become large; this would change the sign of $\partial \bar{\phi}_k / \partial k |_{k_F(t)}$ at the Fermi level and makes the collision dynamics holelike instead of electronlike (see Ref. [35]). One may also be tempted to attribute the emergence of a positive Q to the contribution of hole carriers coming from the TTF chains, as fluctuations and the onset of a pseudogap on TCNQ chains grow. However, other transport measurements on TTF-TCNQ have shown that at ambient pressure the Hall coefficient becomes more negative in the same temperature range, pointing to the still dominant contribution of electron carriers of TCNQ chains [20,36].

We can now look in Fig. 6 at the temperature dependence of Seebeck coefficient for TTF-TCNQ under pressure, as obtained by Weyl *et al.* [25] up to 12.5 kbar. From the figure we see that pressure steadily decreases the amplitude and the slope of the Seebeck coefficient in the high temperature region, where it appears only weakly temperature dependent at high pressure values. Following the example of the situation found at ambient pressure, a more rapid decrease of the amplitude of the Seebeck coefficient is observed at all pressures below $T \sim 150$ K, which evolves toward a change of sign of Q at the approach of the critical temperature T_c. This incursion into the positive region becomes less pronounced with pressure and gives way to a sharp upturn back to high negative values close to T_c.

For the comparison with the present calculations, we first note that in this pressure range, the critical temperature T_c observed for TCNQ chains varies little under pressure and remains relatively close to the ambient pressure value of 54 K [25,37]; T_c has then been kept approximately constant in the calculations. Regarding the fluctuations scale T_c^0, there is no available data concerning its pressure evolution. However, given the empirical relation $T_c \sim T_c^0/3$, which is found in

practice when both temperature scales are accessible, T_c^0 will then be taken to fall in the same range $T_c^0 \sim 150$–200 K used at ambient pressure and in Figs. 4 and 5. The comparison must also go through a readjustment of the electron concentration ρ and the longitudinal hopping $t_\parallel$ with pressure. Both quantities increase following the modification of the charge transfer and intermolecular distances under pressure and lowering temperature due to the high compressibility of a system like TTF-TCNQ [20,23,26,38]. As discussed in Sec. IV B, in our constant-volume calculations, we will consider their average variations under pressure and temperature which are congruent with the relation $\delta \ln \rho \simeq 0.36 \, \delta \ln t_\parallel$ established for TTF-TCNQ [25,38,39]. This is the variation used in Fig. 5 and which cover about 13 kbar of pressure.

Under pressure the observed decline in the amplitude and slope of Q are relatively well caught by the calculations of Fig. 5 in the high temperature domain, although at the highest pressures the experimental temperature dependence shown in Fig. 6 becomes rather weak, making hard the distinction, within experimental accuracy, between a nearly constant behavior and T linearity with a strongly reduced slope. As for the change of regime in the Seebeck coefficient observed for all pressures below 150 K or so, it is only apparent in the calculations of Fig. 5 up to intermediate values of ρ and $t_\parallel$, above which the contribution of collisions is predicted to be small, excepted sufficiently close to T_c.

Regarding the change of sign of Q observed above the true T_c under pressure, it is not reproduced by the present calculations, at least along the line $\rho(t_\parallel)$ of the $(\rho, t_\parallel)$ plane used in the calculations of Fig. 5 (see also Ref. [35]). A possible explanation for this discrepancy may reside in the appreciable temperature variation of the electron concentration in a compressible system like TTF-TCNQ, which is not properly taken into account in constant volume calculations. Such a variation could introduce a continuous drift in the position of the Fermi points toward the position for the minimum of the scattering time as a function of k (see Fig. 2), which would induce a change of sign in the collision term Q_c. In the present framework, this would indicate that in practice Q_c remains sufficiently important when approaching the critical temperature region. Finally, as pressure increases, the sharpening of the upturn of $|Q|$ due to critical scattering close to T_c is fairly well reproduced by calculations of Fig. 5.

VI. CONCLUDING REMARKS

In this work the temperature dependence of the Seebeck coefficient has been calculated for correlated quasi-one-dimensional metals dominated by charge density wave fluctuations. A functional integral method was used for the description of low energy CDW fluctuations ascribed to the precursors of the Peierls superstructure. As the source of inelastic scattering for carriers, these fluctuations were embodied in the numerical solution of the linearized Boltzmann equation which governs the dynamics of scattering time near the Fermi surface. The related corrections to the linear-T dependence of the SC could thus be obtained and assessed as a function of the strength of fluctuations. The analysis was carried out for typical parameters of low-dimensional organic metals, like the two-chain compound TTF-TCNQ, for which the negatively

charge carriers of TCNQ chains undergo a Peierls instability against the formation of a CDW superstructure.

The calculations show that the size of SC corrections linked to the scattering dynamics are congruent with those seen in experiments for TTF-TCNQ, reproducing certain experimental features in the temperature dependent SC at ambient and finite pressures. However, calculations fail to reproduce the incursion of SC towards positive values at the approach of the critical CDW temperature, at least for the model parameters that most realistically fit to TTF-TCNQ [35].

As to the origin of the change of sign, one can invoke the possibility that CDW fluctuations also affect the thermodynamic term Q_0 of the SC in (31). Such corrections were ignored in the present work. Fluctuations can modify the energy dependence of the density of states and carrier velocity near the Fermi level and then transform an electronlike band into a holelike one. However, although the presence of an electron pseudogap induced by fluctuations is visible on the TCNQ chains, as shown by the corresponding Knight shift spin susceptibility [40], it is likely to be too small an effect to lead the needed modifications in the energy dependence of electron velocity that would yield an effective change in the sign of the carriers. This is borne out by measurements of the Hall coefficient, which still displays strongly negative values in the temperature domain where SC becomes positive [36]. This brings us back to the energy dependent scattering time considered throughout this work as the most plausible cause of this change of sign. Remember that for compressible molecular compounds such as TTF-TCNQ, both electron bandwidth and band filling evolve with decreasing temperature [20]. These variations cannot be taken into account accurately in constant-volume calculations like those developed above. Such variations may be responsible for the small shift of the Fermi point needed to transform electron type scattering into hole one.

The applicability of the present theory of the Seebeck coefficient to other quasi-1D fluctuating Peierls systems is rather straightforward, requiring only modifications of electronic band and fluctuations scales. Among them, let's mention for instance the two-chain Peierls compounds TMTSF-DMTCNQ [41] and TTF[Ni(dmit)$_2$]$_2$ [42,43], for which the temperature and pressure dependence of the Seebeck coefficient in the fluctuating metallic phase presents similar features to those discussed in the present work for TTF-TCNQ.

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[35] It is worth noting that the critical fall off of Q towards large negative values is not systematically found for all $t_\parallel$ and $\rho < 1$ when $T \to T_c$. There are actually ranges of values in the $(\rho < 1, t_\parallel)$ plane that depart slightly from the line, $\delta \ln \rho \simeq 0.36 \, \delta \ln t_\parallel$, used in Fig. 5 for TTF-TCNQ, and for which Q changes sign and becomes holelike with large positive values as $T \to T_c$.

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