Thermoelectric power of the narrow-band Hubbard chain at arbitrary electron density: Atomic limit*

Gerardo Beni[†]

Department of Physics, University of California, Los Angeles, California 90024

We study the thermoelectric power of a narrow-band Hubbard chain with an arbitrary number of electrons per site. The calculations are carried out to the lowest order in the transfer integral. We find a characteristic electron density ($\rho = 2/3$) below which the thermoelectric power is negative at all temperatures. In contrast, for $\rho > 2/3$, the thermoelectric power is small and negative only above a characteristic temperature, below which there is a change of sign and slope. We comment on the applicability of these results to the charge-transfer salts of tetracyanoquinodimethan (TCNQ).

I. INTRODUCTION

Recent measurements by Chaikin et al.[1] of the thermoelectric power of the organic conductors tetrathiofulvalinium-tetracyanoquinodimethan (TTF-TCNQ) and quinolium TCNQ have stimulated a new interest in the study of the thermoelectric power of many-body systems. In particular, Maki[2] has investigated the behavior of the thermoelectric power in the fluctuation region above the superconducting transition temperature for one- and two-dimensional systems. Patton and Sham[3] are studying the thermoelectric power of a one-dimensional electron-phonon system near the Peierls transition. In addition, the thermoelectric power of the Hubbard-Holstein Hamiltonian, Eq. (18), has been calculated by Bari[4] to the lowest order in the bandwidth. The thermoelectric power was found to vanish. More generally it has been recently established[5] that a particle-hole symmetric interacting electron system has zero thermoelectric power at all temperatures. This holds for crystals with one electron per lattice site and applies in particular to the half-filled-band one-dimensional Hubbard model.

As is well known, this model has been applied[6] to the charge-transfer salt N-methylphenazinium TCNQ (NMP-TCNQ) which, apart from other interesting properties, exhibits a characteristic temperature dependence of the thermoelectric power. The thermoelectric power is small and negative above 200 °K with an almost linear temperature dependence, which is suggestive of a metallic system. The slope changes below 200 °K and at about 150 °K the thermoelectric power becomes positive, which has been interpreted within the framework of a metal-insulator transition.

The analysis of the thermoelectric power given in Ref. 6, as stressed by the authors themselves, was a crude first guess based on a Fermi-liquid approach and motivated by the lack of an adequate transport theory. On the other hand, the argument could be given some credibility, insofar as the calculated transfer integral agreed in magnitude with that obtained from the Pauli susceptibility and from the analysis of other low-temperature properties. However, this sort of Fermi-liquid analysis cannot be applied to the half-filled-band Hubbard model for which, as we have mentioned, the thermoelectric power vanishes.

This fact seems to add something to the increasing evidence[7-9] which favors a rejection of the simple Hubbard chain as a model for NMP-TCNQ. On the other hand, one may try to investigate appropriate modifications of the model, which could lead to a more consistent description of the properties of NMP-TCNQ. Along these lines some attempts have recently been made. In our group we have investigated the role played by electron-phonon interactions[10] and by long-range Coulomb forces.[11] In this paper we study still another aspect of the deviation from the half-filled-band Hubbard chain, namely the thermoelectric power at arbitrary electron density.

Apart from the question of the applicability to NMP-TCNQ, the variable-density Hubbard chain is a model of intrinsic interest. Recent studies include the high-temperature thermodynamic[12] ground-state energy and zero-temperature susceptibility[13] and low-lying excitations.[14] The transport properties have been rather less studied. To our knowledge the only two works on the subject are those of Ref. 15. In the present paper we derive an expression for the thermoelectric power to zero order in the hopping parameter t [see Eq. (1)]. A subsequent paper has been devoted to the analysis of higher-order terms.[16]

II. THERMOELECTRIC POWER

Let us restrict our attention to a linear chain with lattice constant a and one electron per site. The electronic system is described by the Hubbard Hamiltonian[17]

$$H = - t \sum_{i\sigma} c_{i\sigma}^{\dagger} c_{i+1\sigma} + \text{h. c.} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \ , \qquad (1)$$

where $c_{i\sigma}^{\dagger}$ $(c_{i\sigma})$ is the creation (destruction) operator for electron at the ith site with spin σ.

In order to calculate the thermoelectric power we shall make use of the Kubo formalism.[18] In terms of the Kubo formulas for the transport coefficients of a many-body system, the thermoelectric power S is written as

$$S = \frac{- S^{(2)}/S^{(1)} + \mu/e}{T} \ , \qquad (2)$$

where e is the absolute value of the electronic charge, μ is the chemical potential, and

$$S^{(1)} = + \tfrac{1}{2} \beta e^2 \int_0^{\infty} \langle vv(\tau) + v(\tau)v \rangle \, d\tau \ ; \qquad (3)$$

$$S^{(2)} = + \tfrac{1}{2} \beta e \int_0^{\infty} \langle Qv(\tau) + v(\tau)Q \rangle \, d\tau \ ; \qquad (4)$$

$$v(\tau) = e^{\tau H} v e^{-\tau H} \ , \qquad (5)$$

while $\langle \cdots \rangle$ means thermal average and $\beta = (KT)^{-1}$ (T is the temperature and K the Boltzmann constant).

Here v and Q are, respectively, the velocity and the energy-flux operators which is convenient to write in the following form:

$$v = \lim_{q \to 0} \frac{1}{\hbar q} \sum_j [n_j, H] e^{iq(ja)} \ , \qquad (6)$$

$$Q = \lim_{q \to 0} \frac{1}{\hbar q} \sum_j [h_j, H] e^{iq(ja)} \ , \qquad (7)$$

where $\sum_j h_j = H$, and q is determined by periodic boundary conditions.

In addition, being interested only in the narrow-band limit, we shall use perturbation theory to evaluate the correlation functions in $S^{(1)}$ and $S^{(2)}$ and retain only the lowest-order term in t. This procedure is obviously correct for any thermodynamic calculation, but, for the transport coefficients, requires some justification. In fact, at first sight it may appear meaningless to evaluate

any transport coefficient within an approximation that restricts the motion of the carriers to hopping between two sites (we shall see below that the lowest order in T is indeed t^2). However, a study made by K. Kubo[19] provides us with the necessary justification for this procedure. Kubo was interested in the optical conductivity at zero temperature and for this he derived an expression for the frequency-dependent conductivity by using the Green's function decoupling scheme originated by Hubbard.[17] Following Kubo's work Bari and Kaplan[8] obtained an expression for the conductivity by perturbation theory to second order in t (the same procedure that we shall use below to evaluate S). Their result agrees with Kubo's Green's function approximation to this order. Furthermore, Bari and Kaplan analyzed the higher-order corrections found by Kubo and pointed out that they do not qualitatively alter the lowest-order results, thus providing the justification for using a considerably less laborious approach.

After these preliminary considerations we proceed in our evaluation of the thermoelectric power and first of all obtain the necessary expression for the velocity and energy-flux operators. From Eqs. (6) and (7) it is easy to derive[4] the following forms:

$$v = \frac{at}{i\hbar} \sum_{i\sigma} (c_{i\sigma}^{\dagger} c_{i-1\sigma} - c_{i\sigma}^{\dagger} c_{i+1\sigma}) \ ; \qquad (8)$$

$$Q = Q_U + Q_t = \frac{Uta}{i\hbar} \sum_{i\sigma} n_{i-\sigma}(c_{i\sigma}^{\dagger} c_{i-1\sigma} - c_{i-1\sigma}^{\dagger} c_{i\sigma})$$
$$+ \frac{t^2 a}{i\hbar} \sum_{i\sigma} (c_{i\sigma}^{\dagger} c_{i-2\sigma} - c_{i\sigma}^{\dagger} c_{i+2\sigma}) \ . \qquad (9)$$

These expressions are exact but in view of our narrow-band approximation, the second term in Q may be dropped at the outset. For the same reason, the full Hamiltonian H may be replaced by the unperturbed Hamiltonian H_0 in the correlation functions of $S^{(1)}$ and $S^{(2)}$. Thus we obtain

$$\frac{e S^{(2)}}{S^{(1)}} = \frac{\int_0^{\infty} d\tau \, \text{Tr}[e^{-\beta(H_0 - \mu \, \Sigma_i n_i)}(Q_U e^{-iH_0\tau} v e^{iH_0\tau} + e^{-iH_0\tau} v e^{iH_0\tau} Q_U)]}{\int_0^{\infty} d\tau \, \text{Tr}[e^{-\beta(H_0 - \mu \, \Sigma_i n_i)} (v e^{-iH_0\tau} v e^{iH_0\tau} + e^{-iH_0\tau} v e^{iH_0\tau} v)]} \ . \qquad (10)$$

Now traces of Eq. (10) may be performed straightforwardly by using

$$e^{-iH_0\tau} c_{j\sigma} e^{iH_0\tau} = e^{iU\tau n_{j-\sigma}} c_{j\sigma} \ , \qquad (11)$$

and by noting that each trace contains the product of two operators linear in t. This allows us to restrict the traces to only two sites and we obtain at once

$$S = - \frac{K}{e} \left(\frac{\beta U x^2}{e^{\beta U} + x^2} - \ln x \right) \ , \qquad (12)$$

where $x = e^{\beta U}$. As expected, for a half-filled band S vanishes because $\mu = \tfrac{1}{2} U$. We should also remark that S is independent of t so that Eq. (12) is effectively the thermoelectric power in the zero-bandwidth limit. The situation is different in the case of the conductivity σ for which only the ratio σ/t^2 can be obtained exactly in the zero-overlap limit.

Next we need an expression for the chemical potential. This is easily found, as we are effectively in the zero-bandwidth limit. In fact, the ground-partition function is simply
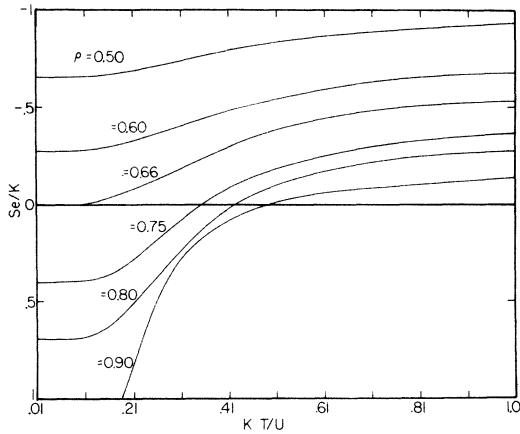
FIG. 1. Temperature dependence of the thermoelectric power at various electron densities.

$$Z = (1 + 2x + x^2 e^{-\beta U})^N = Z^N \;\;, \tag{13}$$

and the number condition

$$\frac{\partial z}{\partial x} = \rho \frac{z}{x} \;\;, \tag{14}$$

where ρ is the electron density; i.e., $\rho = N_e/N$ where N_e is the number of electrons. From (13) and (14) we get at once

$$x = \frac{-(1-\rho) + [(1-\rho)^2 + \rho(2-\rho)e^{-\beta U}]^{1/2}}{e^{-\beta U}(2-\rho)} \;\;, \tag{15}$$

which, together with Eq. (12), completes the calculations of S.

It is interesting to note that β and U appear as a factor in the thermoelectric power so that S is essentially a function of only one parameter. In particular we make the following remarks. The thermoelectric power for the semiconductors with hopping conductivity has been calculated by a number of authors[20] in the case of noninteracting carriers. In this case

$$S = \frac{-K}{e} \ln \frac{2-\rho}{\rho} \;\;. \tag{16}$$

We see thus that Eq. (16) is the limiting case of Eq. (12) for $KT \gg U$.

More interesting is the opposite limit, i.e., $U \gg KT$. In this case Eq. (12) reduces to

$$S = \frac{-K}{e} \ln \frac{2|1-\rho|}{\rho} \;\;, \tag{17}$$

which changes sign for $\rho > \frac{2}{3}$. This signals the crucial role placed by correlation effects for almost half-filled systems.

Further insight is gained by the analysis of the

curves reproduced in Fig. 1. Here we have plotted the thermoelectric power as given by Eq. (12) for various densities in the low-temperature (strong-correlation) regime. At low densities correlation effects are not crucial but the nearly half-filled case is remarkably affected by the intra-atomic Coulomb repulsion. The interesting fact is that S tends to zero as ρ tends to 1 always changing its sign at a temperature of the order of $\frac{1}{2} U$.

III. CONCLUSION

As we have seen in Sec. II, the quasi-half-filled narrow-band Hubbard chain exhibits a thermoelectric power qualitatively similar to that of NMP-TCNQ. Moreover, the order of magnitude of the thermoelectric power is in agreement, for $\rho = 0.9$, with the NMP-TCNQ data. Also the temperature of the $S = 0$ point is of the correct order of magnitude. In addition, the $\rho = 0.5$ case agrees satisfactorily at high temperatures with recent measurements[21] of the thermopower of quinolinium TCNQ. On the contrary, it has been shown that various plausible extensions of the half-filled Hubbard model do not lead to any finite thermoelectric power. This is the case, for example, of the extended Hubbard Hamiltonian H_e with long-range Coulomb interaction $H_e = H + \sum_{ik} v_{ik} n_i n_{i+k}$. Moreover, the inclusion of electron-phonon interaction does not lead necessarily to loss of particle-hole symmetry and thus finite thermopower. An example is provided by the Hubbard-Holstein Hamiltonian H_{HH}

$$H_{HH} = H + \hbar\omega \sum_i b_i^\dagger b_i - B \sum_i x_i n_i \;\;;$$

$$x_i = (\hbar/2M\omega)^{1/2}(b_i + b_i^\dagger) \;\;, \tag{18}$$

where $b_i^\dagger$ (b_i) are creation (destruction) operators for a quantum $\hbar\omega$ on the localized oscillator of effective mass M. However, if an electron-phonon term of the form considered in Ref. 10, i.e., $-A \sum_i x_i n_{i\sigma} n_{i-\sigma}$ is taken into account in Eq. (18), then the particle hole symmetry is destroyed. Thus it is difficult to decide which (if any) modification of the half-filled Hubbard model will give the correct thermoelectric behavior of NMP-TCNQ and we believe that further understanding will be gained by the analysis of higher-order terms in t.

[*]Supported in part by the Office of Naval Research and National Science Foundation.

[†]IBM Predoctoral Fellow.

[1]P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973).

[2]K. Maki (unpublished).

[3]B. Patton and L. J. Sham (unpublished).

[4]R. A. Bari (unpublished).

[5]G. Beni and C. Coll, Phys. Rev. B (to be published).

[6]A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 942 (1972).

[7]D. Cabib and T. A. Kaplan, Phys. Rev. B 7, 2199 (1973).

[8]R. Bari and T. A. Kaplan, Phys. Rev. B 6, 4623 (1972).

[9]D. J. Klein, W. A. Seitz, M. A. Butler, and Z. G. Soos (unpublished).

[10]P. Pincus, Solid State Commun. 11, 51 (1972); U.

Bernstein and G. Beni, Phys. Rev. B (to be published).

[11]G. Beni and P. Pincus, Phys. Rev. B (to be published).

[12]G. Beni, P. Pincus, and D. Hone, Phys. Rev. B 8, 3389 (1973); M. Plischke (unpublished).

[13]H. Shiba, Phys. Rev. 136, 930 (1972).

[14]C. Coll, Phys. Rev. B (to be published).

[15]R. A. Bari, D. Adler, and R. V. Lange, Phys. Rev. B 2, 2898 (1970); G. Beni, T. Holstein, and P. Pincus, Phys. Rev. 138, 312 (1973).

[16]J. Kwak and G. Beni (unpublished).

[17]J. Hubbard, Proc. R. Soc. A 276, 238 (1963).

[18]R. Kubo, J. Phys. Soc. Jpn. 12, 1203 (1957).

[19]K. Kubo, J. Phys. Soc. Jpn 31, 30 (1971).

[20]See for example Shchegolev, Phys. Status Solidi 12, 9 (1973) and references quoted therein.

[21]P. Chaikin, J. Kwak, and G. Beni (unpublished).