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Hartree theory for the negative-U extended Hubbard model. II. Finite temperature

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The zero-temperature Hartree theory is extended to finite temperature to investigate the phase diagram, the order parameters, and the chemical potential of the negative-U extended Hubbard model in the weak-coupling regime. All the transitions between the charge-ordered, the singlet-superconducting, the mixed, and the nonordered phases are second order. In a special region of the parameter space, we discover the heat-charge-order process, which is the main source for the qualitative difference between the results of the present weak-coupling regime and the strong-coupling regime investigated earlier. Phenomena associated with the heat-charge order are compared to other work in which an effect similar to the heat-charge order exists.

I. INTRODUCTION

Several authors have suggested the possibility of short-range effective electron-electron attraction as a result of the coupling between electrons and intramolecular vibrations or electronic excited states,[1-4] or between electrons in different bands in a chemical complex.[5] In Si-inversion layer, White and Ngai[6] conjectured the polaronic and bipolaronic effects as the origin of such effective attraction.

Most theoretical analyses on this subject were carried out in terms of the Hubbard-type model Hamiltonian with attractive intra-atomic correlation (negative U).[7-25] The Hubbard-type model with attractive intra-atomic interaction has been applied to amorphous materials,[26-29] to inorganic compounds with mixed valences,[5,30] and to metals in polar insulators.[31]

Investigation on negative-U systems has progressed rapidly in the last two years, both experimentally and theoretically. Negative-U properties have been found or proposed for point defects in silicon[32-34] and in glasses,[35-37] for a Si-inversion layer,[38,39] for interstitial boron in silicon,[40] and for states in the gap in hydrogenated amorphous silicon.[41] Negative U may also be the possible mechanism of superconductivity in glasses,[42] in nonsimple metals[43] and in metal-semiconductor interface.[44,45]

Recently we have derived the Hartree ground-state phase diagram for the negative-U extended Hubbard model in the weak-coupling limit.[46] In this paper we will extend the diagram to finite temperature and study its thermodynamic properties. The present results will then be compared to those for strong-coupling limit which we obtained earlier.[47]

II. THEORETICAL ANALYSIS

In an earlier paper[46] (referred to as I) we have derived the Hartree formalism which will be used in the present calculation. Let us first briefly summarize the results. Consider the extended Hubbard model with negative U,

$$H=\sum_{ij\sigma}{}' t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\frac{U}{2}\sum_{i\sigma}n_{i\sigma}n_{i-\sigma}+\tfrac{1}{2}\sum_{ij\sigma\sigma'}{}' W_{ij}n_{i\sigma}n_{j\sigma'}-\mu\sum_{i\sigma}n_{i\sigma}\,, \tag{1}$$

where σ is the spin index, and the other subscripts label the N atomic sites. For simplicity only the Coulomb energy W_{ij} is included in the interatomic interaction. If ϵ_k and W_k are, respectively, the Fourier transforms of t_{ij} and W_{ij}, then (1) can be expressed in the Bloch representation

$$H=\sum_{k\sigma}(\epsilon_k-\mu)c_{k\sigma}^{\dagger}c_{k\sigma}+\frac{1}{2N}\sum_{kk'q\sigma\sigma'}(W_q+U\delta_{\sigma-\sigma'})c_{k+q\sigma}^{\dagger}c_{k\sigma}c_{k'-q\sigma'}^{\dagger}c_{k'\sigma'}\,. \tag{2}$$

The Bogoliubov upper bound of the free energy[48]

$$F_0 = -\frac{1}{\beta}\ln\{\mathrm{Tr}[\exp(-\beta H_0)]\} + \langle H - H_0\rangle_0 + \mu N_e \tag{3}$$

can be obtained with a proposed trial Hamiltonian H_0. In the above equation $\beta = 1/k_B T$, N_e is the number of electrons, and $\langle \cdots \rangle_0$ is the thermal average with respect to H_0. It has been pointed out that the ground state of H exhibits no magnetic ordering.[46,47] For the present work we are not interested in the heat magnetization.[49] We then only need to introduce a charge-order parameter Δ and a singlet-superconducting-order parameter X. If we restrict ourselves to systems which can be separated into two interpenetrating sublattices A and B, the trial Hamiltonian can be expressed as

$$\begin{aligned} H_0 = {} & \sum_{k\sigma}(\epsilon_k - \mu - A_0)c^\dagger_{k\sigma}c_{k\sigma} \\ & - \tfrac{1}{2}\sum_{k\sigma}(\Delta c^\dagger_{k\sigma}c_{k+Q\sigma} + \mathrm{H.c.}) \\ & + \tfrac{1}{2}\sum_{k\sigma}(X c^\dagger_{k\sigma}c^\dagger_{-k-\sigma} + \mathrm{H.c.})\,, \end{aligned} \tag{4}$$

where A_0, Δ, and X are variational parameters to minimize the free energy F_0. In the above equation $\vec{\mathrm{Q}}$ is a vector to differentiate the two sublattices such that $\exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}}) = 1$ if $\vec{\mathrm{R}}$ belongs to A and $\exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}}) = -1$ if $\vec{\mathrm{R}}$ belongs to B.

The energy spectrum of H_0 consists of four branches

$$A_k^{\pm} = [(E_k \pm \bar{\mu})^2 + |X|^2]^{1/2}\,, \tag{5}$$

where $E_k = (\epsilon_k^2 + \Delta^2)^{1/2}$, $\bar{\mu} = \mu + A_0$, and k is restricted to the inner half of the first Brillouin zone. In terms of the eigensolutions of H_0 the minimal F_0 is then obtained as

$$\begin{aligned} F_0/N = {} & \bar{\mu}(n-1) + \frac{(U+2ZW)n^2}{4} \\ & - \frac{\Delta^2}{(U-2ZW)} - \frac{|X|^2}{U} \\ & - \frac{1}{\beta N}\sum_k \left[\ln\left[\frac{2\cosh\beta A_k^+}{2}\right] \right. \\ & \left. + \ln\left[\frac{2\cosh\beta A_k^-}{2}\right]\right]\,, \end{aligned} \tag{6}$$

where $ZW = -W_Q$ and Z is the coordination number. The gap parameters Δ and X,

$$\Delta = (2ZW - U)n_Q/2\,, \tag{7}$$

$$X = -Ux_0 \tag{8}$$

are functions of the corresponding order parameters n_Q and x_0,

$$\begin{aligned} n_Q &= \frac{1}{N}\sum_{k\sigma}\langle c^\dagger_{k+Q\sigma}c_{k\sigma}\rangle_0 \\ &= \frac{\Delta}{2N}\sum_k\left[\left[1+\frac{\bar{\mu}}{E_k}\right]B_k^+ + \left[1-\frac{\bar{\mu}}{E_k}\right]B_k^-\right]\,, \end{aligned} \tag{9}$$

$$x_0 = \frac{X}{4N}\sum_k (B_k^+ + B_k^-) \tag{10}$$

of the charge-ordered (CO) and the singlet-superconducting (SS) states, respectively. The third variational parameter A_0 is related to the electron density

$$\begin{aligned} n &= \frac{1}{N}\sum_{k\sigma}\langle c^\dagger_{k\sigma}c_{k\sigma}\rangle_0 \\ &= 1 + \frac{1}{2N}\sum_k[(E_k+\bar{\mu})B_k^+ - (E_k - \bar{\mu})B_k^-] \end{aligned} \tag{11}$$

as

$$A_0 = -(2ZW + U)n/2\,. \tag{12}$$

In the above equations, $B_k^{\pm} = (A_k^{\pm})^{-1}\tanh(\beta A_k^{\pm}/2)$.

For given values of U, W, n, and the band structure ϵ_k, we solve Eqs. (7)–(11) self-consistently for tently for Δ, X, and the chemical potential $\bar{\mu}$ (or n_Q, x_0, and μ). The CO and the SS phases correspond to solutions $\Delta \neq 0$ but $X = 0$ and $X \neq 0$ but $\Delta = 0$, respectively. If both $X \neq 0$ and $\Delta \neq 0$, we have the mixed (M) phase. Finally, solution with $\Delta = X = 0$ gives the nonordered (NO) phase.

The ground-state properties have been studied in I by setting $T = 0$ in the above equations. It is then possible to solve the pure (CO, SS, and NO) phases analytically. However, for $n \neq 1$ and $W > 0$, the solution for the M phase must be derived numerically using a model density of states. For a square density of states

$$\rho(E) = \begin{cases} \dfrac{1}{2D} & \text{for } |E| < D \\ 0 & \text{otherwise} \end{cases} \tag{13}$$

the ground state has the following properties:

(1) The ground state is SS for $n \neq 1$ and $W \leq 0$ as well as for $n = 1$ and $W < 0$.

(2) The ground state is CO for $n=1$ and $W>0$.

(3) The ground state is degenerate in SS, CO, and M phases for $n=1$ and $W=0$.

(4) For $n\neq 1$ and $W>0$, with fixed values of U and W, there is a second-order transition from the M to the SS phases as $|n-1|$ increases.

In this paper we will continue to investigate the finite-temperature properties using the same square density of states.

In some cases the coupled equations (7)–(11) reduce to simpler forms. Let us first consider the case $n=1$. From (11) we have $\bar{\mu}=0$, and so for all phases (9) and (10) can be simplified as

$$\frac{\Delta}{2ZW-U}=\Delta G(\beta,\Delta^2+|X|^2)\,, \tag{14}$$

$$-\frac{X}{U}=XG(\beta,\Delta^2+|X|^2)\,, \tag{15}$$

where

$$G(\beta,\alpha^2)=\frac{1}{2N}\sum_k(\epsilon_k^2+\alpha^2)^{-1/2}\times\tanh\left[\frac{\beta}{2}(\epsilon_k^2+\alpha^2)^{1/2}\right]. \tag{16}$$

The free energy F_0/N now becomes

$$\begin{aligned}\frac{F_0}{N}&=\tfrac{1}{4}(2ZW+U)-\frac{\Delta^2}{U-2ZW}-\frac{|X|^2}{U}\\&\quad-\frac{2}{\beta N}\sum_k\ln\left[\cosh\left[\frac{\beta}{2}(\epsilon_k^2+\Delta^2+|X|^2)^{1/2}\right]\right]\\&=\left[\frac{F_0}{N}\right]_{\text{NO}}-\frac{\Delta^2}{U-2ZW}-\frac{|X|^2}{U}\\&\quad-\int_0^{\theta}G(\beta,\xi)d\xi\,,\end{aligned} \tag{17}$$

where $\theta=\Delta^2+|X|^2$ and $(F_0/N)_{\text{NO}}$ is the free energy of the nonordered phase. It is obvious from (14) and (15) that the M phase exists only if $W=0$. Then, the three CO, SS, and M phases are degenerate, and

$$\left[\frac{F_0}{N}\right]_{\text{CO,SS,M}}-\left[\frac{F_0}{N}\right]_{\text{NO}}=\frac{-\alpha^2}{U}-\int_0^{\alpha^2}G(\beta,\xi)d\xi\,, \tag{18}$$

where $\alpha^2=\Delta^2$, $|X|^2$, and $\Delta^2+|X|^2$ for the CO, SS, and M phases, respectively. With fixed value of U, we have

$$\begin{aligned}\frac{d}{d\beta}&\left[\left[\frac{F_0}{N}\right]_{\text{CO,SS,M}}-\left[\frac{F_0}{N}\right]_{\text{NO}}\right]\\&=-2\alpha\left[\frac{1}{U}+G(\beta,\alpha^2)\right]\frac{d\alpha}{d\beta}-\int_0^{\alpha^2}\frac{\partial G(\beta,\xi)}{\partial\beta}d\xi\\&=-\int_0^{\alpha^2}\frac{\partial G(\beta,\xi)}{\partial\beta}d\xi\leq 0\,.\end{aligned} \tag{19}$$

It has been shown in I that for the ground state ($\beta=\infty$), $(F_0/N)_{\text{CO,SS,M}}-(F_0/N)_{\text{NO}}$ is negative. With the help of (15) and (16), we see that $(F_0/N)_{\text{CO,SS,M}}-(F_0/N)_{\text{NO}}$ approaches zero as $\beta\rightarrow 0$. Consequently, $(F_0/N)_{\text{CO,SS,M}}-(F_0/N)_{\text{NO}}$ is always negative as long as the degenerate CO-SS-M phase exists. So for $n=1$ and $W=0$ the only transition is from the degenerate CO-SS-M phase to the NO phase.

If $n=1$ but $W\neq 0$, M phase does not exist and we obtain from (17)

$$\left[\frac{F_0}{N}\right]_{\text{SS}}-\left[\frac{F_0}{N}\right]_{\text{NO}}=\frac{-|X|^2}{U}-\int_0^{|X|^2}G(\beta,\xi)d\xi\,, \tag{20}$$

$$\left[\frac{F_0}{N}\right]_{\text{CO}}-\left[\frac{F_0}{N}\right]_{\text{NO}}=\frac{-\Delta^2}{(U-2ZW)}-\int_0^{\Delta^2}G(\beta,\xi)d\xi\,. \tag{21}$$

Since we know from I that $(F_0/N)_{\text{SS}}\leq(F_0/N)_{\text{NO}}$ and $(F_0/N)_{\text{CO}}\leq(F_0/N)_{\text{NO}}$ for the ground state, as long as the ordered phases exist, these inequalities then also hold for all temperatures. It is trivial to see from (16) that $\partial G(\beta,\alpha^2)/\partial\alpha^2\leq 0$. Hence, for given values of W, U, and β, the values of Δ and $|X|$ determined from $(1/2ZW-U)=G(\beta,\Delta^2)$ and $(-1/U)=G(\beta,|X|^2)$ are related as $\Delta\gtrless|X|$ if $W\gtrless 0$. We can then write

$$\left[\frac{F_0}{N}\right]_{\text{SS}}-\left[\frac{F_0}{N}\right]_{\text{CO}}=\frac{-|X|^2}{U}+\frac{\Delta^2}{(U-2ZW)}-\int_{\Delta^2}^{|X|^2}G(\beta,\xi)d\xi \tag{22}$$

and similarly prove

$$\frac{d}{d\beta}\left[\left[\frac{F_0}{N}\right]_{\rm SS}-\left[\frac{F_0}{N}\right]_{\rm CO}\right]=-\int_{\Delta^2}^{|X|^2}\frac{\partial G(\beta,\xi)}{\partial\beta}d\xi \gtrless 0 \text{ if } W \gtrless 0\,. \tag{23}$$

Since for the ground state $(F_0/N)_{\rm SS}-(F_0/N)_{\rm CO}\gtrless 0$ if $W\gtrless 0$, again the same relation holds for all temperatures as long as these phases exist. This is indeed the situation shown by our numerical solution, and so for $n=1$ the transition is from the SS (CO) to the NO phases if $W<0$ ($W>0$).

For the general case $n\neq 1$, it has been proved in I that the M phase does not exist at any temperature if $W\leq 0$. For the pure phases we only need to solve one equation for the NO phase, and two for both the CO and the SS phases. With a square density of states, via a numerical solution we found the only transition being from the SS to the NO phases. Therefore, the ground-state ordered phases in (1)–(3) listed below Eq. (13) go directly to the NO phase with increasing temperature. Such simple transition is not so interesting, and we will now investigate only the interesting case $n\neq 1$ and $W>0$.

The numerical solution for $n\neq 1$ and $W>0$, as will be shown in the next section, indicates that for given values of U/D and ZW/D all four phases appear in the k_BT/D vs $|n-1|$ phase diagram. A study on the order parameters reveals that all the transitions between various phases are second order. For second-order phase transition, we can derive very simple expressions for the phase boundaries between the SS-NO and the CO-NO phases. In the next section we can use such simple expressions to check the accuracy of the self-consistent numerical solutions.

To obtain the SS-NO transition temperature $\beta({\rm SS})$ for given values of U/D, W/D, and $|n-1|$, we have to solve (8), (10), and (11) self-consistently by letting $X\rightarrow 0$. For a square density of states, we arrive at the simple equation

$$\frac{1}{U}=-\frac{1}{4D}\int_{-D}^{D}(E-\bar{\mu})^{-1}\times\tanh[\tfrac{1}{2}\beta({\rm SS})(E-\bar{\mu})]dE\,, \tag{24}$$

where

$$\bar{\mu}=D+\frac{1}{\beta({\rm SS})}\ln\left[\frac{1-e^{-n\beta({\rm SS})D}}{e^{(2-n)\beta({\rm SS})D}-1}\right]. \tag{25}$$

Equation (24) is very easy to solve numerically. For the special case of weak coupling $2D\beta({\rm SS})\gg 1$, the chemical potential $\bar{\mu}$ can be approximated by its zero-temperature value $(n-1)D$ given in I. Then the integral of (24) can be carried out analytically to yield

$$\beta({\rm SS})=\left[\frac{\pi}{2\gamma D\sqrt{n(2-n)}}\right]\exp\left[\frac{-2D}{U}\right] \tag{26}$$

where $\gamma=1.78$ is the Euler constant. Using the zero-temperature result of X given in I as an approximation, we obtain

$$\frac{1}{\beta({\rm SS})X}\simeq\frac{\gamma}{\pi}\simeq 0.57\,, \tag{27}$$

the same relation as in the BCS theory. On the other hand, at the strong-coupling limit $|U|\gg 2D$ the energy band is very narrow and so a good approximated solution can be derived from (24) and (25) as

$$\beta({\rm SS})=\frac{2\ln[n/(2-n)]}{|U|(n-1)}\,. \tag{28}$$

Using the zero-temperature result of I, we found that at the strong-coupling limit $1/\beta({\rm SS})X(T=0)$ varies between 0.5 and 0.64 as n increases from 1 to 1.85. Combining this with the weak-coupling formula (27), we discover

$$\frac{1}{\beta({\rm SS})}\simeq 0.57\times X(T=0)$$

as a good interpolation (as compared to the numerical result in the next section) between the strong- and the weak-coupling limits. However, we must emphasize that the Hartree theory is not valid at the strong-coupling regime.

The simple expression for the CO-NO transition temperature $\beta({\rm CO})$ can be derived from (7), (9), and (11) in a similar fashion. In terms of the square density of states (13), we get

$$\frac{1}{2ZW-U}=\frac{1}{4D}\int_{-D}^{D}\frac{1}{E}\tanh\left[\frac{1}{2}\beta({\rm CO})(E-\bar{\mu})\right]dE \tag{29}$$

where

$$\bar{\mu}=D+\frac{1}{\beta({\rm CO})}\ln\left[\frac{1-e^{-n\beta({\rm CO})D}}{e^{(2-n)\beta({\rm CO})D}-1}\right]. \tag{30}$$

But unfortunately it is impossible to obtain a simple formula for the transition temperatures across the SS-M and the M-CO boundaries. These have to be calculated numerically by locating the minimum free energy.

III. NUMERICAL RESULTS

Based on the square density of states (13), (7)–(11) are solved numerically for all the four phases with given values of U/D, W/D, and $|n-1|$. The stable phase is then determined by comparing the free energies of various phases via (6). The chemical potential $\bar{\mu}$ [which is related to the true chemical potential μ by $\bar{\mu}=\mu-n\times(2ZW+U)/2$] and the order parameters of the stable phase are also calculated. Since we are interested in the change of phase diagram with rising temperature, the range of $|n-1|$ is the same as that for the zero-temperature phase diagram in I.

The $k_BT/D-|n-1|$ phase diagrams are shown in Fig. 1 for $ZW/D=0.11$, 0.33, 0.55, and 0.77 and $-U/D=0.4$ (dotted curves), 0.8 (dashed curves), 1.2 (solid curves), and 1.6 (dashed-dotted curves). It is interesting to compare these phase diagrams for weak coupling to those for strong coupling given in Ref. 47. Though the characteristic features of the phase diagrams in both the weak- and the strong-coupling regimes are similar, the transition temperatures for the weak coupling are proportional to U while for the strong coupling they are proportional to $1/U$. A special feature of the weak-coupling case is observed near the multicritical point when ZW/D is comparable or greater than $-U/D$, namely, a transition SS→NO→CO→NO with increasing temperature for fixed $|n-1|$. Analogous to the heat magnetization phenomena, here we obtain a heat-charge-order process associated to the NO→CO transition. This heat-charge order is a consequence of the Hartree theory where the β(CO) depends on both W and U, but β(SS) depends on U only. For the strong-coupling case investigated in I, there is no such heat-charge order. We will return to this point for further discussion in the next section.

In Fig. 2 we show the CO order parameter (thin-lined curves) and the SS order parameters (heavy-lined curves) for $ZW/D=0.55$ with various values of $|n-1|$ marked in each panel. Again the dotted, the dashed, the solid, and the dashed-dotted curves correspond to $-U/D=0.4$, 0.8, 1.2, and 1.6, respectively. The SS order parameter behaves qualitatively similar to that for the strong-coupling regime.[47] However, the CO order parameter behaves rather differently in both limits. In the CO phase see a broad maximum in Fig. 2, in contrast to the monotonic decrease with increasing temperature in the case of strong coupling. The postion of the broad maximum moves toward the M-CO phase boundary as $-U$ gets larger. In the M phase the present result of the CO order parameter does not decrease monotonically with

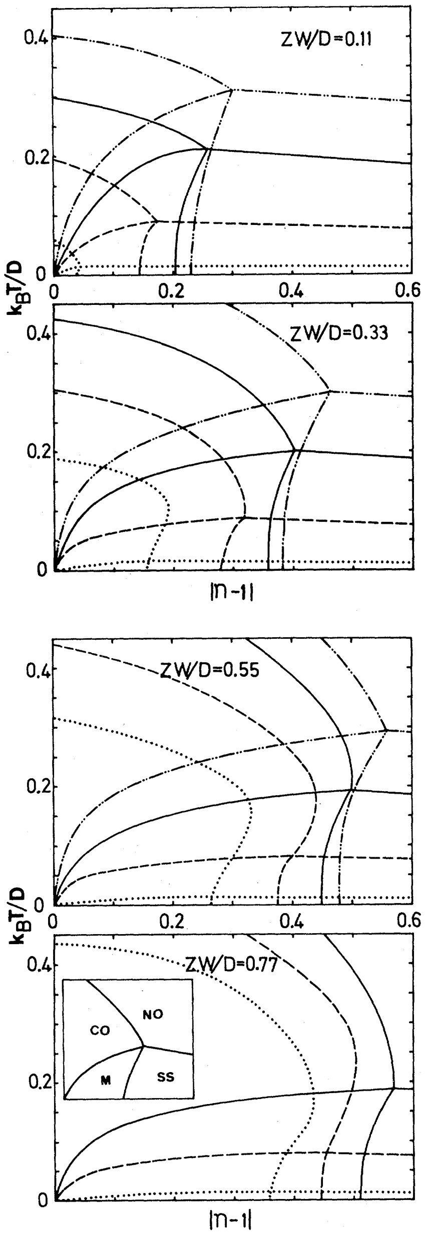

FIG. 1. Phase diagram for $-U/D=0.4$ (dotted curves), 0.8 (dashed curves), 1.2 (solid curves), and 1.6 (dashed-dotted curves). Relative positions of the four phases are illustrated by the inset in the panel of $ZW/D=0.77$.

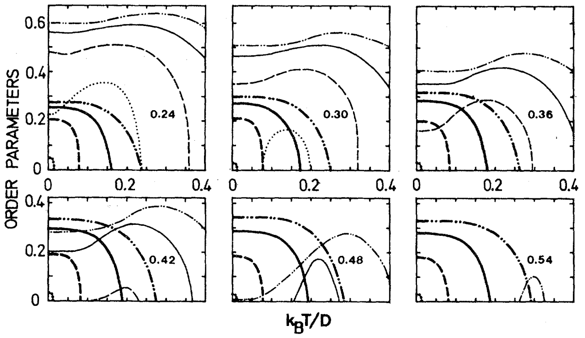

FIG. 2. SS order parameter (heavy-lined curves) and CO order parameter (thin-lined curves) for $ZW/D=0.55$ and value of $|n-1|$ marked in each panel. Same specification of $-U/D$ values as in Fig. 1.

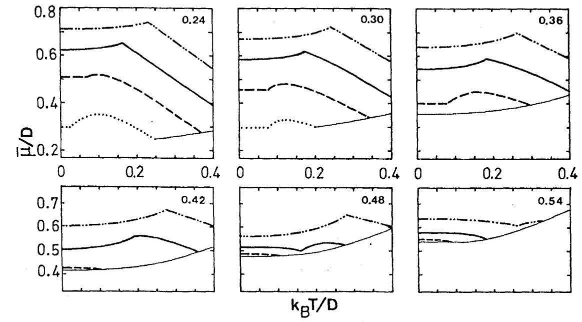

FIG. 3. Chemical potential for $ZW/D=0.55$ and value of $|n-1|$ marked in each panel. Same specification of $-U/D$ value as in Fig. 1.

the lowering of temperature as shown by the CO order parameter in Ref. 47. In Ref. 47 the CO order parameter exhibits a cusp at the M-CO phase boundary. Whether a cusp also appears in the present calculation we cannot answer, because due to the extreme time-consuming nature of the numerical calculation, we did not take a small enough temperature step. In a mean-field-approximation study on the Peierls transition in a quasi-one-dimensional model, Ono[50] also obtained the similar behavior of the order parameter. It is worthwhile to point out that the heat magnetization in the Hubbard model has been examined by Schumacher *et al.*[51] The characteristic feature of the order parameter exhibiting the heat magnetization in their work is exactly the same as that of our CO order parameter in the temperature region where the heat-charge order occurs. Finally, from the continuous behavior of the order parameters, all the phase transitions are second order.

The chemical potential corresponding to the six cases in Fig. 2 is given in Fig. 3. Both the dotted and the thin-solid curves are for $-U/D=0.4$. Since the $\bar{\mu}$ plotted here is related to the true chemical potential μ as $\bar{\mu}=\mu-n(2ZW+U)/2$ in the NO phase, $\bar{\mu}$ is independent of W and U. Hence for any value of U the chemical potential in the NO phase is also represented by the thin-solid curve. Let us first compare these results with those given in Ref. 47 for strong coupling. We notice that in the M phase the temperature dependence of $\bar{\mu}$ is qualitatively the same in both cases. In the SS phase for the strong-coupling limit $\bar{\mu}$ is temperature independent but in the present calculation it has a weak temperature dependence. If $-U/D$ is about two times ZW/D or larger, the characteristic feature of $\bar{\mu}$ in the CO phase of Fig. 3 is the same as that for the strong-coupling regime. However, when $-U/D$ reduces to a value comparable to $2ZW/D$, a broad maximum of $\bar{\mu}$ associated uniquely to the weak coupling begins to appear in the CO phase. At zero temperature the true chemical potential μ in the M phase is n independent for the strong-coupling limit, but not so for the weak coupling. To close up this section we should mention that the effective chemical potential obtained by Ono[50] has similar behavior as our $\bar{\mu}$ in the CO and the NO phases.

IV. FINAL REMARKS

Although we have discovered many common features to both the strong- and the present weak-coupling regimes, it will be useful to comment on a few key points. For the electron density $n=1$, the system remains insulator when the CO phase is stable. As the temperature is raised to β(CO), an insulator-to-metal transition occurs. However, if the coupling is strong, the high temperature phase is still nonmetallic, since in this case the NO phase consists of uncorrelated electron pairs. The CO phase is still characterized by an energy gap even if $n\neq1$, but at the Fermi energy there is a finite number of carriers which can support current. The existence of such carriers is due to the fact that the wave vector of the charge order becomes incommensurate to the lattice periodicity. We should stress that for our model Hamiltonian the CO phase is stabilized by the positive interatomic interaction W. Therefore, the value of W strongly affects the physical properties of the CO phase. For example, with increasing W, both Δ and β(CO) increase and the CO phase expands towards the higher value of $|n-1|$. We have not calculated the conductivity, thermoelectric power, and the magnetic susceptibility of the CO phase. Nevertheless, we expect them to be qualitatively similar to those derived with the commensurate-Peierls-distortion model with $n\neq 1$,[50] judging from the mathematical equivalence of the effective Hamiltonians describing the CO phase in both cases.

In the present paper the treatment of the SS phase follows the same line as the BCS theory, except that the electron pairing is allowed for all the $\vec{k}$ states in the whole Brillouin zone. Thus the pair-breaking mechanism is enhanced as compared to the BCS theory. This may also be the reason that unlike the BCS theory, in the present result the gap to critical-temperature ratio $X\beta$(SS) depends on the electron density n slightly. In the strong-coupling regime we have found earlier[47] that the temperature at which electron pairs begin to form is different from the condensation temperature. However, in the weak-coupling regime, these two temperatures merge into one. On the other hand, for both the strong- and the weak-coupling cases, the SS phase is stable for an arbitrarily small value of n. Whether this is a consequence of the mean-field-type approximation or of the band-structure effect remains to be checked.

The competition between the CO and the SS phases results in the M phase in both the strong- and the weak-coupling limits. Since the weight of the SS component in the M phase increases as the temperature gets lower, one expects the appearance of the superconducting feature while going from the metallic CO phase ($n\neq 1$) to the M phase with decreasing temperature. This conjecture agrees with model analysis of Balseiro and Falicov[52] on layer compounds $1T$-TaS$_2$ and $2H$-NbSe$_2$, as well as with the experimental data of transition-metal dichalcogenides and $A15$ compounds.[53]

The essential difference between the strong- and weak-coupling regimes emerges in the form of heat-charge order in the Hartree theory. The broad maxima in both the CO order parameter and the $\bar{\mu}$ just reflect the existence of such heat-charge order. Therefore, it is important to know whether the heat-charge order is a genuine phenomenon associated to the model Hamiltonian. It is possible that the heat-charge order is due to the use of a simple square density of states, or due to the retaining of a single-order parameter X_Q with $Q=0$ in the trial Hamiltonian H_0, or due to the application of the molecular-field approximation, or due to the neglect of other more complicated charge orders (even incommensurate). A detail analysis to check these possibilities should be very valuable.

We have mentioned in the Introduction that experimental findings suggest the existence of negative-U centers in various materials. The most relevant ones to the present model analysis seem to be $\mathrm{BaPb}_{1-x}\mathrm{Bi}_x\mathrm{O}_3$ and $\mathrm{Cs}_2\mathrm{SbCl}_6$. The former has been recently discussed in terms of the real-space electron pairing[54] whereas the latter gives strong evidence for the CO phase induced by the negative correlation energy.[55] However, a direct comparison between the theory and the experimental data requires first the inclusion of the disorder effect and the extension of the theory to the intermediate-coupling regime.

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