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Commensurate-incommensurate transitions in coupled chain systems at 0 K

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We study the theory for the structure of coupled incommensurate chains in the weak-coupling limit. Both chains are deformable. The emphasis is on the commensurate-incommensurate transition. In this limit, the structure is described in terms of commensurate domains separated by walls which have intrachain—and interchain—interactions. It is argued that the latter cause defects of one chain to be pinned on defects of the other, so that the commensurate-incommensurate transition is in general complicated and exhibits a behavior reminiscent of the devil's staircase. We show that crystals formed from interpenetrating chains may have different types of commensurate-incommensurate transitions, depending on whether one sublattice only forms defects (walls) at the transition, or both simultaneously. In the last section we discuss the fluctuations of defect planes at low temperatures in quasi-one-dimensional conductors.

I. INTRODUCTION

In linear-chain compounds with segregated chains of donors and acceptors, it often happens that the periods of the donor and acceptor chains are not simply related.[1] The materials consist of two interpenetrating incommensurate sublattices. Under certain circumstances (with pressure, or upon varying stoichiometry, or else) the two sublattices can undergo a commensurate-incommensurate transition.

Previous theoretical studies[1] have considered models with a three-dimensional (3D) array of two types of chains a and b, with each chain surrounded by nearest neighbors of type B and vice versa. Each chain experiences a rigid external periodic potential due to its neighbors. This approximation (the external potential approximation, EPA) allows a direct connection with the problem studied by Frank and Van der Merwe[2] some 30 years ago. In the latter work the linear chain of atoms in a periodic external potential (which also simulates an adsorbed layer in a substrate) is replaced by an elastic continuum, in which case an exact solution is obtained. As the period of the external potential is varied and approaches the natural period of the chain, a continuous transition to the commensurate state occurs, in which the period of the chain and the external potential are the same. A continuous transition is also obtained in the adsorbed layer problem when the chemical potential for the adsorbed atoms is varied.

The continuous character of the transition can be best described by the distance between defects (which are one-dimensional dislocations) which separate commensurate domains. This distance goes continuously to infinity at the transition in the continuum model. The continuum model is a legitimate one when the size of a defect is large in comparison with the interatomic distance. When such is not the case, the discreteness of the lattice must be explicitly taken into account.[3] Exact results on specific simple models show that in general defects become pinned by the lattice potential, and hysteresis results: defect motion can only occur with dissipation. In the particular case of a harmonic chain with nearest-neighbor forces and a periodic substrate, the atomic mean distance at constant pressure is constant each time its ratio to the substrate period is a rational number. As pressure is varied, this interatomic mean distance is a monotonous increasing function which has infinitely many steps. It is called a devil's staircase.[3] Similar complicated phase diagrams are currently discussed in the literature[4] for other models such as Ising models with nearest-neighbor interactions. This paper investigates the statics of coupled chain problems, concentrating on a particularly interesting limit, that of the commensurate-incommensurate transition. In contrast to the external potential approximation, we are interested in cases when both chains are deformable. We do not attempt to reach exact solutions of this complicated problem. We chose to base our work on the simple idea that in the commensurate-incommensurate limit, everything can be described in terms of commensurate domains separated by walls, which have intrachain interactions and interchain interactions as well. Throughout this work the coupling between chains is assumed to be weak in comparison with intrachain elastic forces.

In Sec. II, we choose to study a somewhat academic model of a frontier between two adsorbed layers of different atomic species on the same substrate. The frontier is described by two chains of different atomic species, each with its own chemical potential, on the same atomic substrate. The substrate is rigid, but both chains, which interact, are deformable. We show that this system exhibits a very complex behavior for the commensurate-incommensurate transition, even though each chain is treated in the continuum approximation. The reason is that the interacting periodic array of defects must be treated in the discrete limit.

In Sec. III we examine the problem of interacting incommensurate chains. In this case each chain experiences the field due to the other one, and no substrate is present. We show that the commensurate-incommensurate transition can exhibit different behaviors: both chains may start forming defects at the transition, or only one at a time. In this case again the behavior of the system near the transition is complicated because of the discreteness of the defect "lattice."

In Sec. IV we comment briefly on the finite temperature behavior of an infinite 3D array of coupled chains near a commensurate-incommensurate behavior: defect planes, which are stable at zero temperature exhibit fluctuations at finite temperatures. We examine those at low temperatures.

II. INTERACTING INCOMMENSURATE CHAINS

In this section, the experimental situation we think of corresponds to that of different species of rare gases physisorbed on a periodic substrate. The simplified model for the frontier between two half-infinite adsorbed layers reduces to two interacting chains of different species of atoms. Admittedly this is a rather academic model; we do not know of any actual experimental situation in the physics of adsorbed layers which could be analyzed in terms of this model. However it is useful to devote some thought to this problem, as it serves as a guide line to the more realistic problem of interpenetrating incommensurate lattices which we will study in Sec. III; each chain is characterized by elastic constants J_a and J_b, natural periods a and b, and chemical potential μ_a^0 and μ_b^0.

The energy for the two chains is

$$\mathcal{H} = \mathcal{H}_a + \mathcal{H}_b + \mathcal{H}_{ab} \ , \tag{1}$$

where

$$\mathcal{H}_i = J_i \sum_{n=1}^{N_i} (x^i_{n+1} - x^i_n - i)^2 - \sum_{n=1}^{N_i} U \cos 2\pi x^i_n/l + \mu_i^0 N_i \ , \tag{2}$$

with $i = a,b$. U is the amplitude of the substrate potential, the period of which is l. We choose $U = U_a = U_b$ for simplicity, without loss of generality. N_i is the number of atoms in the ith chain and x^i_n is the position of the nth atom in the ith chain. In this paper we shall only consider the problem in the continuum limit, which amounts to say that for both chains, the characteristic length

$$r_i = \frac{i}{\pi}\left(\frac{J_i}{2U}\right)^{1/2} >> 1 \ .$$

$\mathcal{H}_{ab}$ is the interaction between chains which we discuss at greater length later in this section.

The problem we discuss is different from that studied by Bak and Timonen.[5] These authors allowed for elastic deformation of the substrates, resulting in a modified interaction between defects in the chain. The substrate cannot have dislocations, it can only respond elastically to dislocations in the chain. In the problem defined by Eq. (1), both chains may have dislocations, as we shall discuss later.

It is convenient to introduce the new variables u_n and v_n defined by

$$x^a_n = np_a l + \frac{l}{2\pi} u_n \ , \quad x^b_m = mp_b l + \frac{l}{2\pi} v_m \ .$$

u_n (and v_n) characterize the displacement of the nth (mth) atom from the bottom of the np_a^{th} (mp_b^{th}) trough of the substrate potential. p_a and p_b are integers such that $p_a l \sim a$ and $p_b l \sim b$. Equations (1) and (2) then become, in the continuum limit

$$\begin{aligned}\mathcal{H} = {} & \frac{J_a l^2}{4\pi^2} \int_0^{N_a} dn \left[\left(\frac{du}{dn}\right)^2 + \frac{4\pi^2 U}{J_a l^2}(1-\cos u)\right] \\ & + \frac{J_b l^2}{4\pi^2} \int_0^{N_b} dn \left[\left(\frac{dv}{dn}\right)^2 + \frac{4\pi^2 U}{J_b l^2}(1-\cos v)\right] \\ & + \frac{J_a l}{\pi}(p_a l - a)(u_{N_a} - u_1) + \mu_a N_a \\ & + \frac{J_b l}{\pi}(p_b l - b)(v_{N_b} - v_1) + \mu_b N_b + H_{ab}(u,v) \ ,\end{aligned} \tag{3}$$

where we have defined a shifted chemical potential

$$\mu_a = \mu_a^0 - U + J_a(p_a l - a)^2 \ ,$$

$$\mu_b = \mu_b^0 - U + J_b(p_b l - b)^2 \ .$$

A. Interaction potential $\mathcal{H}_{ab}$

We now discuss the interaction between chains. In the present problem, it is reasonable to assume that an atom of a given chain has harmonic interactions with the nearest neighbor in the opposite chain.

However one must be more specific: the coupling must be such that the nth atom in one chain has the same interaction with atoms in the other chain if they have identical relative positions, irrespective of their initial position along the chain (i.e., their position for very weak elastic forces). In other words the interaction potential must be periodic with period l. A simple form for the interchain interaction which meets the above mentioned requirements is

$$\mathcal{H}_{ab}=\lambda\sum_{\langle n,m\rangle}\sin^2[\tfrac{1}{2}(u_n-v_m)] \ ,$$

where λ is a constant and the sum $\langle n,m\rangle$ is restricted to all pairs of nearest-neighbor atoms which sit within the same segment of length equal to the substrate period centered around each atom (see Fig. 1).

In the continuum limit, $\mathcal{H}_{ab}$ reduces to

$$\mathcal{H}_{ab}=\lambda\int dx\,\sin^2\{\tfrac{1}{2}[u(x)-v(x)]\} \ . \tag{4}$$

This form reduces to a harmonic potential when $u(n)-v(n)<<\pi$. It also ensures that two atoms with the same distance have the same interaction energy, irrespective of the total displacement of each atom along its chain, as it should. This choice is by no means unique, but it is a physically reasonable one. Furthermore it is isomorphic with interchain couplings introduced for the study of quasi 1D conductors within the Landau-Ginzburg picture.[6] We do not believe that any of the results discussed in this paper depend crucially on the particular form chosen here for $\mathcal{H}_{ab}$.

We now seek solutions $u(n)$ and $v(n)$ which minimize Eq. (3). The resulting Euler-Lagrange equations are

$$\begin{aligned}\frac{d^2u}{dn^2}&=2\frac{\pi^2U}{l^2J_a}\sin u+\frac{\pi^2}{l^2}\frac{\lambda}{J_a}\sin(u-v) \ ,\\ \frac{d^2v}{dn^2}&=2\frac{\pi^2U}{l^2J_b}\sin v+\frac{\pi^2}{l^2}\frac{\lambda}{J_b}\sin(v-u) \ .\end{aligned} \tag{5}$$

Equation (5) is the equation for two coupled pendula, the "time" being the distance along the chain, and the coupling term being a sinusoidal coupling. A trivial solution for Eq. (5) is $u=v=0$. This corresponds to both chains commensurate with the substrate

$$x_n^a=np_al \ , \quad x_m^b=mp_bl \ .$$

We know from the single chain treatment[2] that this is possible if $U>U_c^a$, U_c^b with $U_c^i=\frac{1}{4}\pi^2J_i(i-l)^2$ for the chain with free ends. In the presence of a fixed chemical potentials[7] which is the case we study in this section, chains are commensurate with the substrate when

$$\mu_i^-<\mu_i<\mu_i^+ \ ,$$

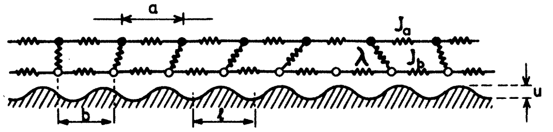

FIG. 1. Coupled chains on a periodic substrate—an atom of one chain interacts only with the nearest atom of the other chain. In the discrete version, some atoms do not interact with atoms of the other chain.

where

$$\mu_i^\pm=2J_il(p_il-i)\pm\omega_i \ .$$

In the absence of interchain coupling

$$\omega_i\equiv\omega_i^0=\frac{4l}{\pi}\sqrt{2UJ_i} \ . \tag{6}$$

In the presence of a weak interchain coupling, i.e., if $\lambda<<u$, it is straightforward to show that ω_i is shifted by the interchain coupling

$$\omega_i=\left(1+\frac{\lambda}{4U}\right)\omega_i^0 \ .$$

We shall limit our discussion to the case of weak interchain coupling.

The general solution of the coupled nonlinear differential Eq. (5) [together with the condition that $\mathcal{H}$ in Eq. (3) is a minimum with respect to integration constants] is hopelessly complicated; however one can give an approximate treatment of this solution in a particularly interesting limit that of the commensurate-incommensurate transition, where the physical picture is dominated by well-defined defects (dislocations[3]) separated by commensurate domains (the so-called "soliton limit"[7]). The question we ask is: How is the commensurate-incommensurate transition affected by the interchain coupling? In the single chain case, the transition is characterized by the behavior of the distance Rl between defects in their periodic array. This varies according to the law

$$|\mu-\mu^\pm|\simeq\text{const}\,\frac{R}{r}\exp-\frac{R}{r} \ . \tag{7}$$

In order to study the two chain problems, we start from the expression of the energy for noninteracting chains in the soliton limit and introduce the coupling as a perturbation. The energy of each chain in the absence of a coupling term in the soliton limit is

$$\mathcal{H}_i=[\omega_i\xi e^{-R_i/r_i}\mp(\mu_i-\mu_i^c)]\frac{N}{R_i}+\mu_i\frac{N}{p_i} \ . \tag{8}$$

In Eq. (8), the exponential term is an interaction term between neighboring defects in the same chain. Indeed, each defect is characterized by a displacement

$$u(n)=\pm4\tan^{-1}(e^{-n/r}) \tag{9}$$

so that it is exponential at large distance from the core. The factor ξ is a positive constant of order 1.

Within this picture, it is clear that a commensurate domain in chain a has zero interaction energy with chain b if the latter is commensurate. The interaction between chains reduces to an interaction between defects. We simplify the problem by taking into account this interaction only between nearest-neighbor defects in different chains which is quite reasonable since the interaction is also exponential at large distance for defects in different chains. Also for simplicity we have computed this interaction for identical defects, i.e., with identical r [Eq. (9)]. In the weak-coupling approximation, the presence of a defect in one chain does not perturb the displacement in the other chain and the interaction energy Γ is simply

$$\Gamma(R)=\int_{-\infty}^{+\infty}\lambda\sin^2\left\{\tfrac{1}{2}[u(x)-v(x+R)]\right\}dx \ . \qquad (10)$$

The result is

$$\Gamma^{--}(R)=\Gamma^{++}(R)=4\lambda r\tanh\left(\frac{R}{2r}\right)\left[\tanh\left(\frac{R}{2r}\right)+\frac{R}{2r}\operatorname{sech}^2\left(\frac{R}{2r}\right)\right] \qquad (11)$$

for interaction between defects of the same sign (two heavy defects or two light ones) and

$$\Gamma^{+-}(R)=4\lambda r\coth\left(\frac{R}{2r}\right)\left[\coth\frac{R}{2r}-\frac{R}{2r}\operatorname{cosech}^2\left(\frac{R}{2r}\right)\right] \qquad (12)$$

for defects of opposite sign. Both functions are shown in Fig. 2. The central points, which are fairly model independent are the following.

Two defects of identical sign have repulsive experimental interaction at large distance which tends to a constant at infinity and exhibit an attractive interaction at very short distance (shorter than the defect size, i.e., $R \ll r$) which goes to zero at zero distance for identical defects. At a distance $R_M \sim r$, (within the present model, $R_M \simeq 0.86r$) the interaction energy goes through a maximum of order $4.3\lambda r$.

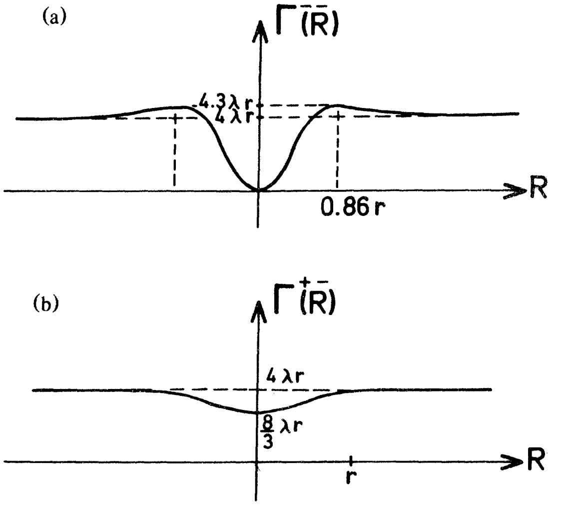

FIG. 2. Interaction energy between two defects on different chains as a function of distance along the chain in the weak-coupling limit. (a) Defects with identical signs, and (b) defects with opposite signs.

Two defects of opposite sign have long-distance attractive exponential interaction, a short-distance ($R \sim 0.6r$ for our model) attractive part, one-third weaker than for defects of the same sign.

Keeping in mind the spirit of the "soliton limit", for which domain sizes are always much larger than the defect size, we substitute for $\Gamma^{++}(R)$ a simplified form shown in Fig. 3, with the exponential part extending to zero distance, and an attractive δ function at zero distance, of depth $4r\lambda$. Likewise for Γ^{+-}, in which case the δ function is also attractive, with appropriate height.

B. Defect configurations

We now study the following problem: Let one chain be in an incommensurate configuration with a regular array of defects of given sign the concentration of which is fixed by the value of the chemical potential, i.e.,

$$R_a = r\ln|\mu_a-\mu_a^{+}| \ . \qquad (13)$$

How does the second chain behave as a function of

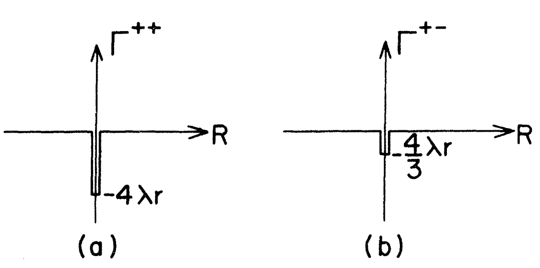

FIG. 3. Simplified model for the defect-defect interactions. (a) Defects with identical signs, and (b) defects with opposite signs.

its chemical potential μ_B? First assume that only a few defects are present in chain b so that $R_b >> R_a$. In that case the lowest energy is obtained when defects in the b chain associate (condense) with defects in the a chain; the elastic interaction between defects in the b chain is of order $(\omega_b/2r^2)\exp(-R_b/r)$, i.e., it is exponentially small. The problem of the configuration of defects in the b chain is similar to that of Frank-Van der Merwe (FVdM) chain, with applied periodic potential of strength $4\lambda r$ and periodicity R_a, so that the characteristic length equivalent to the defect size in the FVdM problem is

$$\rho \sim R_a \left[\frac{\omega_b}{2} \frac{1}{r^2} \exp\left(-\frac{R_b}{r} \right) \Big/ 8\lambda r \right]^{1/2} .$$

This is much smaller than R_a except for vanishingly small interchain interaction

$$\lambda < \lambda_c \sim (\omega_b/16r^3)\exp - (R_b/r) ,$$

when $\lambda > \lambda_c$, it is unphysical to treat the problem in the continuum limit. Therefore the theoretical framework to discuss the variation of R_b with μ_b is that of the discrete limit.[3] Physically, defects in the b chain sit in the potential well of the a chain with a distance $R_b' = qR_a$ with q integer defined by $R_b/R_a = q + \alpha$ $(\alpha < 1)$. Isolated defects of b defects compensate for the fact that R_b is not the equilibrium distance corresponding to μ_b. Such defects also lower the chain energy by sitting in the attractive potential well of a defect in the a chain. Therefore one concludes that the critical potential $\mu_b^c = \mu_b^{0c}$; in that limit the interchain interaction vanished from μ_b^c. We have implicitly assumed until now that the defect equilibrium distance in chain a was unaltered in the presence of b defects. In reality, the equilibrium distance R_a changes with the concentration of b defects. The calculation of this effect is easy in the limit $R_b >> R_a$. The critical chemical potential μ_a^+ is shifted from $\mu_a^+ = \mu_a^{0+} + 2\lambda r$ to $\mu_a^+ = \mu_a^{0+} + 2q\lambda r/(q-1)$ and the equilibrium distance

$$R_a' = \ln|\mu - \mu_a^+| = \ln|\mu - \mu_a^{0+} - 2\lambda r(1-q^{-1})|$$

(valid for $q >> 1$) when μ_b varies to increase R_b, the behavior becomes complicated, but a simple solution is obtained for $R_b = R_a (q=1)$. In that case, obviously,

$$R_b = R_a = r \ln|\mu_a - \mu_a^{+0}| = r \ln|\mu_b - \mu_b^{+0}| .$$

For that particular case, the interchain interaction does not affect the value R_a or R_b, and operates only to cause defects to order two by two. Thus we have a qualitative understanding for the behavior of the chain a in the presence of the chain b with defects. If the distance between a defects is held fixed, the results of Ref. 3 apply in a straightforward manner: the behavior of R_b as a function of μ_B is described by a devil's staircase.[3] However, because in fact R_a changes with μ_b, no exact result is available at present. It is clear that the actual behavior must be reminiscent of the devil's staircase; in particular, we expect the system to exhibit hysteresis due to dissipative effects during defect motion.[3]

When μ_b continues to vary so as to increase the defects density in b chain, the distance between defects in the a chain stays constant as soon as $R_b < R_a$; all defects in the a chain are then coupled to defects in the b chain, so that

$$R_a = r \ln|\mu_a - \mu_a^{+0}| .$$

As a consequence, Aubry's results apply rigorously for $R_b > R_a$, since the defect-defect interaction within a chain is quadratic (convex function) and the interchain interaction potential is symmetric and periodic.

In that case the defect mean distance R_b for a given μ_b is constant each time R_b/R_a is a rational number. $R_b(\mu_b)$ is a monotonous increasing function which has infinitely many steps and is called a devil's staircase. Notice that we are referring to the mean distance between defects, not to that between atoms. For $R_b << R_a$, only a fraction $1/q' \sim R_b/R_a$ of defects in the b chain are coupled to defects in the a chain. Thus the average distance between b defects is given by

$$R_b \sim r \ln\left| \mu_b - \mu_b^+ + \frac{2\lambda r}{q'} \right| .$$

C. Defects of different sign in chains *a* and *b*

When $\mu_a > \mu_a^+$ while $\mu_b < \mu_b^{0-}$, defects in chains a and b have opposite sign. The only significant differences are (1) the attractive part of the exponential interchain interaction, and (2) the potential well for zero distance is about $\frac{1}{3}$ of that for defects of identical sign.

Therefore the previous discussion carries over to this case with minor obvious changes: the critical μ_b is shifted from μ_b^{0-} by an amount equal to $\frac{4}{3}\lambda r$, etc. Because the interchain interaction potential is weaker, the binding energy of defects is smaller (by a factor 3) and hysteresis effects are accordingly of minor amplitude.

III. COUPLED INTERPENETRATING CHAINS

In this section we study a problem related to that studied in the previous section, that of coupled interpenetrating chains such as can be found in linear chain compounds with segregated chains of donors and acceptors, such as (TTF) $(SCN)_{0.545}$, $(TTF)I_{0.714}$, $(TTF)_2I_{3-\delta}$,[1] mercury chain compounds,[8] etc. This problem was studied by Theodorou and Rice.[1] They considered a crystal with a chain structure such that two incommensurate sublattices exist with periods a and b, respectively. The two lattices are taken to be oppositely charged and bound together by electrostatic forces. The periods a and b are determined by minimizing the combined intrachain energy, charge-transfer energy and the Madelung energy due to the long-range Coulomb attraction between chains.

Because of the different periodicities, different sites on the same chain will experience different potentials. It was shown in Ref. 1 that each chain experiences from the rest of the crystal a periodic potential of strength

$$\begin{aligned} U_a &= 4Q_aQ_bz_b(bd)^{-1/2}\exp(-2\pi d/b) \ , \\ U_b &= 4Q_aQ_bz_a(ad)^{-1/2}\exp(-2\pi d/a) \ , \end{aligned} \tag{14}$$

where $Q_{a,b}$ are the charges of the ions belonging to sublattices a and b, respectively. d is the fixed distance between chains. $z_{a,b}$ is the number of (a,b) nearest-neighbor chains to chain (b,a). The potentials U_a and U_b play the role of the substrate potential studied in the last section. The period of the potential felt by one chain is that of the other chain.

It is clear from Eq. (14) that chains with very different periods a and b experience very different potentials, so that, as was done in Ref. 1, one may study in that case one chain in the presence of a rigid undeformable potential. However, in reality, and expecially when $a \sim b$, both chains are allowed to distort. This two-sublattice problem was studied in Ref. 1 within the so-called EPA approximation. The latter which amounts to replace in the chain potential the undistorted lattice period by the average period of the distorted lattice, is valid far from the commensurate-incommensurate transition. Near the latter, the concept of an average period becomes invalid, as each chain is formed of commensurate domains separated by walls. Our purpose is to investigate the chain configuration in this limit. We shall start from a simple commensurate situation where both chains have identical period $\tilde{a} = \tilde{b}$ and we study how the system goes over to the incommensurate situation.

When $\tilde{a} = \tilde{b}$, we have $U_a = U_b = U(\tilde{a})$. We first find the value of $\tilde{a}$. The energy for two coupled chains is $H_a + H_b$ with

$$H_i = \tfrac{1}{2} J_i \sum_n^{N_i} (x_{n+1} - x_n - a)^2 + \tfrac{1}{2} U(\tilde{a}) \sum_n^{N_i} \left[1 - \cos\frac{2\pi}{\tilde{a}} x_n\right] \ . \tag{15}$$

Minimizing $H_a + H_b$ with respect to $\tilde{a}$ for the commensurate phase $(x_n = n\tilde{a})$ we have obviously

$$J_b(\tilde{b} - b) = J_a(a - \tilde{a})$$

(remember $b < \tilde{b} < \tilde{a} < a$) so that

$$\tilde{a} = \tilde{b} = \frac{J_b b + J_a a}{J_b + J_a} \ . \tag{16}$$

Now let us investigate the condition for appearance of defects (solitons) in this system.

We are dealing with the "free-end" chain problem studied in the single-chain case by FVdM.[2] Thus defects appear upon varying the strength of the potential U. By straightforward application of the standard formula, the critical potentials for appearance of defects in either chain would be

$$U_a^c = \tfrac{1}{8}\pi^2 J_a(\tilde{b} - b)^2 \ , \tag{17a}$$

$$U_b^c = \tfrac{1}{8}\pi^2 J_b(\tilde{a} - a)^2 \ , \tag{17b}$$

so that, using Eqs. (17)

$$U_a^c / U_b^c = J_b / J_a$$

(this last result holds for any commensurate configuration near commensurability $\frac{1}{1}$).

Thus the commensurate-incommensurate transition for coupled interpretating chains seems to exhibit a two-step character, as a function of U, as shown in Fig. 4. Defects first appear on one chain, the other chain being without defects. Then defects of opposite sign appear on the second chain and lock on the defects of the first chain.

We show on Fig. 5 the energy of a defect in one chain in the presence of a defect of, respectively, identical or opposite sign in the other chain, as a function of the distance between defects. The variation of energy of a defect in chain a in the presence of a defect in chain b is

$$\Gamma(R) = \tfrac{1}{2} U \int_{-\infty}^{+\infty} \left[1 - \cos\left(\frac{2\pi}{\tilde{a}}[x_n - y_n(R)]\right)\right] dn \ ,$$

where x_n and $y_n(R)$ are, respectively, the displacement fields in chain a and b, with the centers of the two defects at a distance R. For simplicity, Fig. 5 is

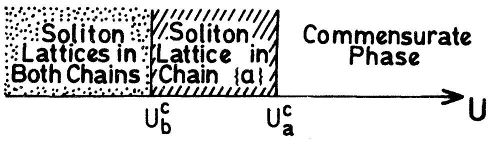

FIG. 4. Schematic phase diagram for the C-IC transition in the interpenetrating chain system. (a) Two-step process, and (b) single-step process, with a finite ratio for the density of defects in one chain and in the other.

drawn, as before, for defects of identical size. Only quantitative changes occur for defects of different size. Comparing Fig. 5 with Fig. 2, we see that in the present problem, the equivalent of the interchain interaction introduced in the previous section is U. Actually, because of the locking potential for defects of opposite sign, the lower critical potential is shifted to a larger value $U_b'^c$, since a defect in one chain locked on a defect in the other chain has smaller energy. We have

$$U_b'^c = 1/(\tfrac{5}{6})^2 U_b^c = 1.44 U_b^c \ . \tag{17c}$$

If $U_a^c > U_b'^c$, the behavior of the coupled chain system is effectively a two-step process (Fig. 4). However, a different situation appears if $U_a^c < U_b'^c$. In the latter case, defects should appear in the b chain as soon as they appear in the a chain. The ratio q of the concentration of b defects over a defects is determined by the condition that defect formation in the a chain lowers the energy, with a concentration $1/q$ of a defects locked on b defects. This condition is found from a modification of Eq. (8). The energy of the chain a in the presence of a concentration $1/q$ of b defects is

$$\epsilon_a = \frac{N}{R_a}(\omega_a - \omega_a^{0c} + \xi\omega_a e^{-R_a/r}) - \frac{N}{qR_a}(\tfrac{1}{6}\omega_a) \ ,$$

with

$$\omega_a = 2\frac{\tilde{b}}{\pi}\sqrt{2UJ_a} \ , \quad \omega_a^{0c} = j_a\tilde{b}(\tilde{b} - a) \ .$$

We find

$$q = \frac{\omega_a}{6(\omega_a - \omega_a^{0c})} = \frac{1}{6(1 - \omega_a^{0c}/\omega_a)} \ .$$

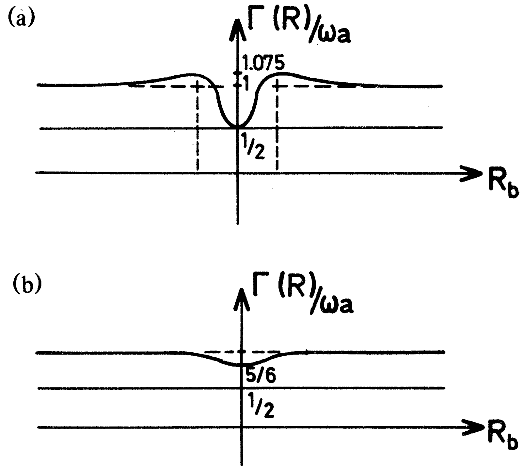

FIG. 5. Energy of a dislocation in one chain in the presence of a dislocation in the other chain as a function of their distance along the chains. (a) Dislocations with identical sign, and (b) dislocations with opposite sign.

This can be rewritten

$$q = \frac{1}{6[1 - \frac{5}{6}(J_a/J_b)^{1/2}]} \ ,$$

when $U_a^c \to U_b'^c = 1.44 U_b^c$, q diverges as $1/[1 - (U_a^c/U_b'^c)^{1/2}]$. Of course the actual value of the ratio J_a/J_b for which q diverges is model dependent. The value $(\frac{6}{5})^2 = 1.44$ found here would change if defects in either chain were allowed to have significantly different sizes. The important point is that depending on the ratio J_a/J_b, the commensurate-incommensurate transition is one of simultaneous occurrence of defects in both chains, or a two-step process, whereby defects first occur in one chain, then in the other. A special case is that of "symmetric" chains, with $J_a = J_b$; in that case the commensurate-incommensurate transition is one of simultaneous occurrence of an equal density of defects of opposite sign coupled one by one.

A. Defect configuration

It is quite hopeless to give a detailed discussion of the defect configuration in the general case; because of the defect interaction, the average distance between defects depends on the concentration of defects in the other chain; both vary in a complicated way when U is varied. It is clear that in all cases there is locking, and hysteresis effects should be present because the problem is always one of the discrete limit. A behavior reminiscent of the devil's stair is likely, with a tendency for R_a/R_b to stay constant each time it is a rational number.

In conclusion, the commensurate-incommensurate transition for coupled interpenetrating chains can exhibit two different behaviors, depending on the ratio of the elastic constants of the two chains. When this ratio is almost one, both chains start forming defects, with a density ratio at the transition given by $q \sim \frac{1}{6} \times [1 - (U_c^a/U_c^{b'})^{1/2}]$. The transition is continuous. For larger values, one chain starts defects, with a distance $R_a \sim \ln|U - U_c^a|$, while the second chain has none, and starts forming its own for a lower value of the interchain potential U.

IV. QUASI-ONE-DIMENSIONAL CONDUCTORS

We now turn to a simple minded extension of the previous discussions to the physics of organic conductors.[9] We have particularly in mind the incommensurate-commensurate transition observed under pressure (~ 15 kbar) in the TTF-TCNQ system.[10] The commensurability is obtained when the Fermi wave vector of the lowest electronic band is $\frac{2}{3}$ that of the zone boundary.[10] Following the microscopic calculation in Ref. 11 for the one-dimensional electron phonon system, we know that at 0 K, the ground state is incommensurate, with a number of solitons per unit length equal to $3\mu/\pi v_F$ where μ is the chemical potential measured from the $\frac{1}{3}$ filling of the electronic band and v_F is the Fermi velocity. A soliton carries $\frac{2}{3}$ excess (or deficit) electron charge. The excess (or deficit) of electrons with respect to the commensurate charge density wave (CDW) in the system is $N(0)\mu$ where $N(0)$ is the density of states at the Fermi level. (Notice that in the conductor problem the dependence of soliton-soliton distance on the chemical potential is not logarithmic.)

Now consider a three-dimensional array of donor and acceptor chains such as TTF-TCNQ. Near commensurability, the density of light solitons with positive charge is equal to the density of heavy solitons with negative charge, for neutrality reasons. The problem is then that of an anisotropic ionic crystal of solitons. The crystal at 0 K has planes of defects separated by commensurate domains of length $\sim \pi v_F/3\mu$. In the single chain case, there is no long-range order in the soliton lattice as long as the temperature is nonzero.[12,13] Such is not the case in the three-dimensional array of coupled chains. Within a Landau-Ginzburg approach one can show that the 3D incommensurate phase sets in at a temperature $T_c \sim \lambda^{1/2}$, where λ is the interchain coupling strength. At low temperature $T < T_c$ and sufficiently near the commensurate-incommensurate transition the soliton lattice forms a system of weakly coupled planar "crystals" of soliton, as stated above. At any finite temperature, each plane exhibits fluctuations normal to its surface, since each "atom" in this plane can only move along its own chain, normal to the surface. A rough qualitative criterion for the existence of the soliton lattice is obtained by writing that the root-mean-square out-of-plane fluctuation length is of the order of the interplane equilibrium distance R. The discussion can proceed along the lines of the standard theory of the roughening transition.[14] Call h_i^μ the distance of a soliton in the ith chain from its zero temperature equilibrium position in the μth plane. The Hamiltonian for the array of coupled planes is

$$E_c(\{h_i^\mu\}) = \frac{1}{2}J \sum_{\substack{i,\delta\\ \mu}} (h_i^\mu - h_{i+\delta}^\mu)^2 + 2H \sum_{\substack{i,\zeta\\ \mu}} (h_i^\mu - h_i^{\mu+\zeta})^2 \ . \tag{18}$$

The sum over δ refers to nearest-neighbor chains of chain i. The sum over ζ refers to nearest-neighbor planes of plane μ. J is due to the elastic force between nearest-neighbor defects of opposite signs [Fig. 2(b)] at small distance. In this rough estimate we assume an interchain interaction $\lambda \sin^2\frac{1}{2}(\phi_n - \phi_{n+\delta})$ [Eq. (4)] as in Ref. 6, i.e.,

$$J = \frac{4}{9}\frac{\lambda}{r} \ . \tag{19}$$

This choice ignores difficulties connected with the long-range character of the Coulomb forces.

In fact expression (18) together with Eq. (19) is strictly valid only for small $h_i < r$. Furthermore, Eq. (18) ignores the strong intrachain repulsions which arise for $h_i^\mu - h_i^{\mu+1} \sim R$, i.e., when defects in the same chain are at short distances. Likewise the "magnetic field" H in Eq. (18) is due to intrachain intersoliton interactions, so that $2H \simeq (\omega\xi/r^2) \times \exp(-R/r)$ [see Eq. (8)].

Equation (18) has a meaning for temperatures such that the defect creation energy is not appreciably changed from its zero-temperature value, i.e., for temperatures much smaller than the Peierls gap: no temperature dependence due to single-particle excitations across the latter is taken into account here. Likewise, Eq. (18) does not take into account any temperature dependence of the order parameter, contrary to the Landau-Ginzburg approach. One should notice that near the commensurate-incommensurate transitions, the "field" H in Eq. (18) vanishes exponentially with the intersoliton distance R. In that sense the problem of weakly coupled chains has become one of weakly coupled planes of defects, since $J/H >> 1$ near the commensurate-incommensurate transition.

Neglect for simplicity the interplane cross term in Eq. (18). Then the partition function for each plane is

$$Z = \prod_q \left(\frac{\pi}{(2/kT)[J(1-\phi(q)) + H]} \right)^{1/2} ,$$

where $\phi(q) = \frac{1}{2}(\cos q_x + \cos q_y)$. It is straightforward from Eq. (18) to show that

$$\begin{aligned} \langle h_i^2 \rangle &= -kT\frac{d}{dH}\ln Z \\ &= -kT\frac{d}{dH}\int q\,dq\, \ln 2\beta[J(1-\phi(q)) + H] \\ &= -kT\int \frac{q\,dq}{J(1-\phi(q)) + H} \sim + \frac{kT}{J}\ln\frac{J}{H} \ , \end{aligned}$$

so that eventually

$$\langle h_i^2 \rangle \sim \frac{kT}{\lambda}R \ . \tag{20}$$

Thus we find that the effective wall fluctuation width at a small finite temperature is inversely proportional to the square root of the interchain coupling, and proportional to the square root of the temperature as well as to the square root of the interwall distance.

Expression (20) loses its meaning when $\langle h_i^2 \rangle \sim r^2$, i.e., when the temperature is larger than $\tilde{T}$ defined by $k\tilde{T}/\lambda R \sim r^2$; i.e., $k\tilde{T} \sim \lambda r^2/R$ in the weak coupling limit $\tilde{T}$ is smaller than the 3D ordering temperature $T_c \sim \lambda^{1/2}$. This is consistent with the statement above that this 3D ordering temperature can be considered as the temperature for which $\langle h_i^2 \rangle \sim R^2$.

However, there is not much point in extending the model to higher temperatures than $\tilde{T}$ since it ignores thermal variation of the order parameter anyway. Furthermore, for $\langle h_i^2 \rangle \sim R$; expression (18) is inadequate since one should take into account the large intrachain contact repulsion between solitons. Very near the commensurate-incommensurate C-IC transition, when defect planes at 0 K are very weakly coupled and one can safely neglect thermal variations of the order parameter at low T, this intrachain contact repulsion is crucial in discussing the order disorder transition which occurs when $\langle h_i^2 \rangle \sim R^2$: the high-temperature phase is a 3D array of coupled 1D liquids of defects; the low-temperature phase is a crystal of weakly coupled planes of defects.

V. REMARKS

The problem of a 2D array of identical weakly coupled chains on a periodic substrate is physically similar to the problem of adsorbed phases on an anisotropic substrate, which has attracted much attention lately.[15,16] In this problem the C-IC transition is dominated by the wall fluctuations, so that the specific heat diverges on the IC side of the transition, but does not on the C side. Note that, in our notation, the correlation length L of an isolated wall in this 2D array of coupled chains is dominated by the interchain coupling through the interchain defect-defect interaction Γ_{ij}. Namely, the average length over which a wall does not fluctuate is $L \sim d \exp(\Gamma_{ij}/kT) = d \exp[(2\lambda r)/kT]$ (defects of the same sign).

VI. CONCLUSION

We have studied a complicated problem with simple minded approximations and have reached a few qualitative conclusions on the subject of interacting incommensurate chains. Even when the continuum limit is valid for a single chain, a complex behavior is expected for interacting incommensurate chains because of interchain defect interactions, which inevitably have the complexity of the discrete limit when defects are sufficiently far away. We have shown that when both chains are deformable the C-IC transition at 0 K may be describable in terms of a devil's staircase, the mean distance between defects being constant each time its ratio to the distance between defects in the other chain is a rational number. Although this holds strictly in the particular case of chains of different atomic species adsorbed on a common substrate, we have argued that a similar behavior is expected in the case of interpenetrating incommensurate lattices, a physically more realistic situation. Finally we have discussed the low-temperature fluctuations of defect planes near the C-IC transition in 3D arrays of conducting chains.

In this paper we have not attempted a close contact with experiments. Although data on modulated structures are available in the literature, observation very near the C-IC transition is scarce or difficult to interpret.[17] Mercury chain compounds[8] do not exhibit any sizable modulation of the cage lattice by the Hg chains (except in the low-temperature 3D regime). One of the best candidates is $(\mathrm{TTT})_2\mathrm{I}_{3-\delta}$. X-ray study undoubtedly shows that displacements in the TTT lattice and the I lattice are coupled. However such studies provide a Fourier transform of the atomic lattice, not of the defect lattice; as is well known the latter is described by a great number of harmonics in the soliton limit.[1] One would need diffraction studies on the defect lattice itself, with photon wavelength of the order of the interdefect distance, i.e., from ultraviolet to intrared light. Such experimental studies are missing at present.

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