

Periodic superstructures in tetrahedrally bonded homopolymers

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Using a lattice sum over single bipolaron potentials displaced by periodicity d , we have analytically obtained a solution for a bipolaron lattice for a tetrahedrally bonded homopolymer within the continuum model of Rice and Phillipot. This solution is used to derive the band structure, which consists of two bipolaron bands symmetrically located about the middle of the band gap in addition to the conduction and valence bands. The electronic density of states, chemical potential μ , and the energy of formation of a bipolaron lattice are also calculated as a function of the bipolaron density ρ_b . The bipolaron chemical potential lies between the conduction-band edge and the upper edge of the upper bipolaron band, indicating that the bipolaron lattice is energetically the most favorable charge configuration at low ρ_b . In the strict weak-coupling limit (infinite momentum cutoff Λ) the bipolaron-bipolaron interaction is found to be repulsive and varies with bipolaron density as $(1/\rho_b)\exp(-2/\rho_b\xi_p)$, ξ_p being the bipolaron characteristic length. Thus, the bipolaron lattice is stable only in the range $0 < \rho_b < 2/\xi_p$. This suggests the possibility of a phase separation of a doped homopolymer into conducting bipolaron droplets at $\rho_b = 2/\xi_p$, while the rest of the system is insulating. Our results apply to polysilylenes, polygermylenes, and their derivatives, as well as to a wide class of carbon-based polymers.

I. INTRODUCTION

The extensive study of quasi-one-dimensional materials, conducting polymers in particular, has contributed significantly in understanding the phenomena of charge-density waves (CDW) in interacting one-dimensional electron-phonon systems.¹ The spinoff of this study has been of even greater significance, for it has yielded clear insights in comprehending the role of nonlinear excitations,^{2,3} namely, solitons, polarons, and bipolarons. These excitations are ubiquitous in a variety of polymer systems. In general, they arise due to the self-trapping of charge leading to the formation of a polaron. In systems with two (or more) degenerate ground states^{4,5} these polarons combine to give domain-wall-like solitons while in systems with a nondegenerate ground state^{6,7} one obtains bipolarons. A bipolaron is a bound state of two polarons and thus contains two charges in a lattice deformation. A common feature of these nonlinear excitations is that they introduce localized states in the (semiconducting) gap.

It has been shown analytically that two solitons⁸ (or two bipolarons⁹) on a polymer chain repel each other with an exponential interaction. Therefore, with increasing electron density (through doping or charge transfer) one obtains periodic superstructures³ such as a soliton lattice (or a bipolaron lattice). In certain systems, for example polyaniline, a polaron lattice may exist.^{10,11} Keeping in view the importance of doped systems a brief review of periodic superstructures in quasi-one-dimensional materials is in order. Ever since a soliton-lattice configuration was found in an approximate numerical study,¹² an exact analytical solution for the soliton lattice^{8,13} has been obtained in a half-filled band $(A)_x$ linearly conjugated polymer such as trans-(CH)_x within

the continuum version⁵ of SSH model.⁴ Later, a soliton-lattice solution¹⁴ was obtained in half-filled band $(AB)_x$ linearly conjugated polymers, e.g., polycarbonitrile, within the Rice-Mele model. The lattice solution was easily generalized¹⁵ to incorporate the case of orbital degeneracy in polyynes as well as spinless fermions describing a spin-Peierls model. In addition, the soliton lattice has been investigated numerically by solving the Fröhlich model in nearly commensurate and incommensurate CDW systems.¹⁶⁻¹⁸ Some examples of materials in this category include TaS₃, NbSe₃, (TaSe₄)₂I, and K_{0.3}MoO₃. Subsequently, several physical properties¹⁹⁻²⁴ of a soliton lattice including optical absorption²⁵⁻²⁷ have been studied.

Similarly, exact analytical solution has been obtained for a bipolaron lattice²⁸⁻³⁰ in both $(A)_x$ and $(AB)_x$ nondegenerate conducting polymers such as *cis*-(CH)_x, polythiophene, polyparaphenylene, etc. within the Brazovskii-Kirova model.⁶ Bipolaron lattice solutions have also been obtained for polymer chains of finite length.³¹ Bipolaron lattices and their physical properties have not been studied as extensively as soliton lattices. The evolution of a lattice from a few bipolarons with increase in the doping can be understood intuitively. An injected charge converts itself into a polaron and eventually into a bipolaron. Therefore, the localized gap states gradually transform into (bipolaron) bands as more charges are injected into the system.

Mainly two techniques have been invoked in the literature to obtain a lattice solution, namely (i) mapping onto a sine-Gordon system in the case of a soliton lattice,⁸ and (ii) the theory of finite band potentials.³²⁻³⁵ The former maps the fermion problem into linear boson oscillations in some unknown potential which is found to be related to the sine-Gordon problem. The latter technique relies

on the theory of the Schrödinger equation whose spectrum has only a finite number of forbidden bands. For a system of functionals to be solvable in the class of finite band potentials it suffices that the system deformation energy be representable in the form of a linear combination of integrals of the Korteweg–de Vries (KdV) equation. In other words, the technique of finite band potentials is an extension of the inverse-scattering formalism of soliton theory which enables the extraction of a self-consistent solution of one-electron equations for a periodic potential and a band structure that has a finite number of gaps. In what follows we employ a much simpler, nevertheless physically appealing, technique of lattice summation^{29,30,36} in which the bipolaron lattice potential is obtained by summing over single bipolaron potentials; each bipolaron being placed a distance d apart from its neighbor on a lattice. We apply this technique to the case of tetrahedrally bonded homopolymers.

Recently the one-electron model of polyenes was extended and successfully applied to describe tetrahedrally bonded homopolymers.^{37,38} Akin to polyenes with nondegenerate ground states these polymers can support polaronlike excitations with localized gap states and infrared vibrational characteristics provided the electron-phonon interaction is not so strong that scission of the polymer occurs. In particular, the excitations include a paramagnetic polaron, a diamagnetic bipolaron, and a charge-neutral polaron, the latter being the relaxed photoexcitation of the polymer.

Saturated polymers such as polysilylenes, polygermylenes, and a wide class of carbon-based polymers constitute some examples of tetrahedrally bonded homopolymers. Furthermore, derivatives of the above including aliphatically substituted silicon, e.g., poly(dimethylsilylene) (PDMS) can also be described by Rice-Phillpot model.³⁷ These polymers have bandgaps in the ultraviolet (uv) region. For instance, the observed energy of maximum uv absorption for an infinitely long chain of poly(organosilylene) (PS) is about 4 eV. In these polymers polarons and bipolarons involve localized regions of reduced bond order. The width of the neutral polaron in the uv-sensitive PS is only a few bond lengths and thus provides a mechanism for energy localization in these polymers. Recently the intragap and intergap optical absorptions in this system were calculated in the presence of polarons and bipolarons.³⁹

The polaron binding energy³⁷ $\epsilon_B(\nu)$ varies as ν^3 , where $\nu=2+\nu_+-\nu_-$ denotes the effective occupation number and ν_+ and ν_- are the occupations of upper and lower localized levels in the gap, respectively. Therefore, there is a strong tendency for two polarons ($\nu=1$) on the same chain to form a bipolaron ($\nu=2$). Thus, at very low doping polarons are expected to be dominant while at low doping bipolarons are present. As we will show *a posteriori* that bipolarons repel each other and hence at moderate doping one would expect a bipolaron lattice. In this paper we obtain an analytic solution for the bipolaron lattice for a tetrahedrally bonded homopolymer within the continuum model of Rice and Phillpot by employing a lattice sum over single bipolaron potentials.

The organization of the paper is as follows. In Sec. II

we first briefly review the electron-phonon continuum model of the saturated homopolymers and summarize the results for the bipolaron. Next, we present a one-to-one correspondence between certain parameters in the model with that of polyenes. This is useful for comparatively interpreting some of the results. In Sec. III we obtain an exact solution for the bipolaron lattice in terms of Jacobian elliptic functions^{40,41} by carrying out a lattice sum over single bipolaron potentials. The lattice solution is shown to satisfy the self-consistency equation. In addition, the complete band structure is obtained. The expressions for energy bands are used to derive the density of states and local electron-charge density distribution in Sec. IV. Next, we make use of the exact solution and the band structure to calculate the energy of formation of the bipolaron lattice in Sec. V. In Sec. VI we calculate the chemical potential of a bipolaron which indicates the stability of the bipolaron lattice. Furthermore, in the strict weak-coupling limit the bipolaron-bipolaron interaction is found to be repulsive. Finally, in Sec. VII we summarize the physical implications of such a lattice particularly the possibility of a phase separation at critical doping density. Relevance to experiments as well as model limitations are also discussed.

II. THE MODEL AND SINGLE (BI)POLARONS

The continuum version of the discrete microscopic model of Rice and Phillpot can be derived³⁸ in the limit in which the spatial inhomogeneities in the bond lengths and bond orders of the polymer vary slowly over microscopic distances, e.g., the lattice constant a . The adiabatic Hamiltonian describing a tetrahedrally bonded homopolymer (in the continuum limit) is then given by

$$\mathcal{H} = \int \frac{dx}{a} \Psi^\dagger(x) \left[\left[-\alpha + \gamma u(x) - \frac{Va^2}{2} \frac{\partial^2}{\partial x^2} \right] \sigma_1 - iVa\sigma_2 \frac{\partial}{\partial x} \right] \Psi(x) + \frac{K_0}{2} \int \frac{dx}{a} u^2(x), \quad (2.1)$$

where $\Psi^\dagger(x) = [A^*(x), B^*(x)]$ is a two-component spinor describing the electron, σ_i are Pauli matrices, $2\alpha = 2(V - \Delta)$ is the covalent energy gap where Δ denotes the matrix element between a and b orbitals on the same atomic site, and $V = V(r_0)$ is the hopping integral between a and b orbitals on the neighboring sites, r_0 being the equilibrium bond length. The first derivative of $V(r)$ with respect to r , evaluated at r_0 , is denoted by γ , and K_0 is the unscreened force constant. $u(x)$ describes the lattice field such that $\gamma u(x)$ is the potential felt by the electrons as a result of $u(x)$. The first term in (2.1) consists of two parts, the electron-phonon interaction energy and the electron kinetic energy. The second term represents the lattice elastic energy. For simplicity of notation, electron-spin index is omitted.

Variation of (2.1) with respect to the spinor components yields the one-electron equations

$$\epsilon_n A_n(x) = \left[-\alpha - \frac{Va^2}{2} \frac{\partial^2}{\partial x^2} + \gamma u(x) - Va \frac{\partial}{\partial x} \right] B_n(x), \quad (2.2a)$$

$$\epsilon_n B_n(x) = \left[-\alpha - \frac{Va^2}{2} \frac{\partial^2}{\partial x^2} + \gamma u(x) + Va \frac{\partial}{\partial x} \right] A_n(x), \quad (2.2b)$$

where ϵ_n denotes the eigenvalues measured relative to Δ_0 , $4\Delta_0$ being the atomic sp^3 promotion energy. The wave functions (electron orbital amplitudes) $A_n(x)$ and $B_n(x)$ are normalized according to

$$\int \frac{dx}{a} [|A_n(x)|^2 + |B_n(x)|^2] = 1. \quad (2.3)$$

The integral extends over $L = Na$, N being the number of monomers on the polymer chain. Furthermore, $A_n(x)$ and $B_n(x)$ must satisfy the self-consistency condition

$$v(x) = \gamma u(x) = - \left[\frac{2\gamma^2}{K_0} \right] \sum_n [P_n(x) - P_n^0] v_n, \quad (2.4)$$

which is obtained by variation of (2.1) with respect to $u(x)$. $P_n(x)$ is the local bond order

$$P_n(x) = \frac{a}{2} [A_n^*(x) B_n(x) + A_n(x) B_n^*(x)] \quad (2.5)$$

and v_n is the occupancy of the n th electronic level. P_n^0 is the bond order in the homogeneous state; $v(x)$ is defined so that $u(x) = 0$ for the homogeneous ground-state semiconductor. The total energy of the system is

$$E = \sum_n v_n \epsilon_n + \frac{K_0}{2} \int \frac{dx}{a} u^2(x). \quad (2.6)$$

The summation in (2.4) and (2.6) indicates a sum over occupied one-electron states.

Equations (2.2) can be decoupled to give a nonlinear Schrödinger equation. Retaining terms to second order with the physical constraint $V \gg \Delta$, one has

$$\left[\epsilon_n^2 - \alpha^2 + v_F^2 \frac{d^2}{dy^2} + 2\alpha\gamma u(y) \right] f_n(y) = 0, \quad (2.7)$$

where $v_F = \sqrt{V\Delta}a$ is the Fermi velocity. Moreover, $y = x + x_0$ and

$$A_n(x) = f_n(x - x_0), \quad B_n(x) = f_n(x + x_0) e^{i\chi_n}. \quad (2.8)$$

The phase χ_n in (2.8) ensures that $A(y)$ and $B(y)$ obey the self-consistency equation (2.4). In view of the consideration that the local electronic density does not change when intragap states are created from the ground state, Eq. (2.4) can be cast in the form

$$\gamma u(x) = \frac{2\gamma^2 a v}{K_0} |f_p(x)|^2, \quad (2.9)$$

where $f_p(x)$ denotes the wave function of the upper intragap state.

Specifically, Eqs. (2.2) and (2.4) have the homogeneous semiconducting ground-state solution $u(x) = 0$ with wave

functions given by plane waves of the form e^{-ikx} and eigenvalues $\epsilon_k^2 = \alpha^2 + v_F^2 k^2$. The wave vector k is measured relative to Fermi vector $k_F = \pi/a$ and is quantized by the condition $kL = 2n\pi$. Soliton solutions are not possible since Eq. (2.4) is not satisfied. Nevertheless, Eqs. (2.7) and (2.9) possess polaron (bipolaron) solutions with the profile

$$u_p(x \pm x_0) = u_0 \operatorname{sech}^2 \left[\frac{x \mp x_0}{\xi_p} \right], \quad (2.10a)$$

where

$$u_0 = \frac{\gamma a v}{2K_0 \xi_p}, \quad \xi_p = \frac{4\Delta K_0 x_0}{\gamma^2 v}, \quad x_0 = \frac{Va}{2\alpha}. \quad (2.10b)$$

ξ_p denotes the characteristic length in this model. The corresponding electronic wave functions are found by solving (2.7) and (2.9) with $u(x)$ given by (2.10). The electronic spectrum consists of two localized levels at $\pm \epsilon_p$ where

$$\epsilon_p^2 = \alpha^2 \left[1 - \frac{v_F^2}{\alpha^2 \xi_p^2} \right] = \alpha^2 \left[1 - \frac{\gamma^4 v^2}{4\Delta V K_0^2} \right] \quad (2.11)$$

and continua with $\epsilon(k) = \pm \omega(k)$ (conduction and valence bands); $\omega(k) = (\alpha^2 + v_F^2 k^2)^{1/2}$. The wave vector k is quantized according to $kL = 2\pi p + \Theta_k$, $p = 0, \pm 1, \pm 2, \dots$ and $\Theta_k = 2 \tan^{-1}(1/k\xi_p)$ is the phase shift experienced by the extended states near the region of a local lattice inhomogeneity (polaron).

The energy of a polaron is given by

$$\begin{aligned} E_p(v) &= \frac{K_0}{2} \int \frac{dx}{a} u_p^2(x) + v\epsilon_p \\ &= \frac{v}{3\alpha} \epsilon^2(v) + v[\alpha^2 - \epsilon^2(v)]^{1/2}, \end{aligned} \quad (2.12)$$

from which the polaron binding energy, $E_B(v) = E(v) - \alpha v \approx v\epsilon^2(v)/6\alpha$. Since $\epsilon_B(v)$ varies as v^3 there is a strong proclivity for two polarons on the same chain to form a bipolaron.

As we noted in the Introduction, the microscopic electron-phonon model for a tetrahedrally bonded polymer is an extension of the one-electron model for polyenes.⁴⁻⁷ Despite the fact that both of these systems possess polaronlike nonlinear excitations, there are certain intrinsic differences which arise due to the nature of bonding in the polymer chain. Homopolymers are characterized by sp^3 hybridized bonding whereas polyenes are described by σ bonding (sp^2 hybrids) in addition to π bonding (p_z). This basic difference affects the nature of solutions (through the self-consistency condition) and therefore the periodic superstructures. However, a comparison between the properties of the two systems is facilitated by noting a one-to-one correspondence between certain parameters of two systems. We already defined the Fermi velocity $v_F = \sqrt{V\Delta}a$. The half-bandgap Δ_0 in polyenes corresponds to $\alpha = V - \Delta$ in homopolymers. Similarly, the shape parameter κ and characteristic length ξ in polyenes are analogs of $1/\xi_p$ and $(V\Delta)^{1/2}a/\alpha$ in homopolymers, respectively.

III. PERIODIC SUPERSTRUCTURES: THE BIPOLARON LATTICE

We noted that Eqs. (2.7) and (2.9) possess single polaron and bipolaron solutions. We now seek periodic solutions of these equations. Our pursuit for periodic solutions is motivated by the fact that at low doping two polarons attract each other to provide a bipolaron.³⁷ With increasing doping the number of bipolarons on the polymer chain increases. One would expect two bipolarons to repel each other with an exponential interaction. Therefore, at intermediate doping the ground state of the system should be a bipolaron lattice. One can resort to the theory of finite band potentials³²⁻³⁵ to obtain the lattice solution. Instead, we employ a direct (infinite) sum over the single bipolaron potentials.^{29,30} This procedure is physically more discernible and entails a simple and direct relationship between certain parameters of the theory with experimentally amenable quantities.

Consider the one-dimensional Schrödinger equation (2.7) with the potential $2\alpha\gamma u_p(y)$ and the profile given by (2.10). The reflectionless potential for a bipolaron can thus be written as

$$V(x) = 2\alpha\gamma u_p \left[\frac{x}{\xi_p} \right] = \left[\frac{2v_F^2}{\xi_p^2} \right] \operatorname{sech}^2 \left[\frac{x}{\xi_p} \right]. \quad (3.1)$$

Next, consider a lattice of bipolarons with a periodicity d . The lattice potential $U(x)$ is then given by

$$U(x) = \sum_{n=-\infty}^{\infty} V(x - nd) = 2\alpha\gamma u_L \left[\frac{x}{\xi_L} \right], \quad (3.2)$$

where $u_L(x/\xi_L)$ and ξ_L are, respectively, the deformation profile and the characteristic length in the lattice problem. ξ_L will be determined from the self-consistency equation (2.9). To perform the lattice sum consider the Fourier-series representation of a cnoidal wave^{42,43}

$$\operatorname{dn}^2(2xK) - \frac{E}{K} = \frac{\pi^2}{K^2} \sum_{n=1}^{\infty} \frac{n \cos(2\pi nx)}{\sinh(\pi n K'/K)}, \quad (3.3)$$

where dn (and sn and cn below) are Jacobian elliptic functions^{40,41} with modulus k . $K(k)$ and $E(k)$ are elliptic integrals of the first and second kind, respectively. $K' = K(k')$ [and $E' = E(k')$ below] where $k' = (1 - k^2)^{1/2}$ is the complementary modulus. Equation (3.3) can be rewritten as

$$\begin{aligned} \operatorname{dn}^2(2xK) - \frac{E}{K} &= \left[\frac{\pi}{2K'} \right]^2 \sum_{n=-\infty}^{\infty} \operatorname{sech}^2 \left[\frac{\pi K}{K'} (x - n) \right] - \frac{\pi}{2KK'}. \end{aligned} \quad (3.4)$$

Using the identity $\pi/2 = EK' + E'K - KK'$ and simple manipulation of elliptic functions, we have

$$\begin{aligned} \sum_{n=-\infty}^{\infty} \operatorname{sech}^2(x - nd) &= \left[\frac{2kK'}{\pi} \right]^2 \left[\frac{E}{k^2K'} - \operatorname{sn}^2 \left[\frac{2K'}{\pi} x \right] \right], \end{aligned} \quad (3.5)$$

with $d = \pi K/K'$. A comparison of Eq. (3.2) with Eq. (3.5) shows

$$U(x) = \left[\frac{2v_F^2}{\xi_L^2} \right] \left[\frac{E'}{k^2K'} - \operatorname{sn}^2 \left[\frac{x}{k\xi_L}, k \right] \right], \quad (3.6a)$$

where

$$\xi_L = \left[\frac{\pi}{2kK'} \right] \xi_p, \quad d = \frac{\pi K \xi_p}{K'} = 2kK \xi_L. \quad (3.6b)$$

Note that the relation [Eq. (3.6b)] between ξ_L and ξ_p will emerge from the self-consistency condition as will be shown later. Since $\operatorname{sn}^2(x, k)$ is periodic with a period of $2K$, $U(x + d) = U(x)$. Thus, $U(x)$ describes a regular array of bipolarons with periodicity d . $U(x)$ oscillates between $(2v_F^2/\xi_L^2)(E'/k^2K')$ and $(2v_F^2/\xi_L^2)(E'/k^2K' - 1)$ as depicted in Fig. 1. Note that $\xi_L > \xi_p$ which indicates that the binding of two charges in a bipolaron in the lattice problem is weaker as compared to an isolated bipolaron.

To determine the band structure and the wave functions of the lattice problem we consider the eigenvalue equation (2.7) with the periodic potential (3.6). Thus the solutions can be labeled by a Bloch wave vector q . Equation (2.7) with (3.6) is Lamé equation⁴⁰

$$\frac{d^2 f_q(\zeta)}{d\zeta^2} = 2k^2 \operatorname{sn}^2(\zeta, k) + A, \quad (3.7a)$$

where

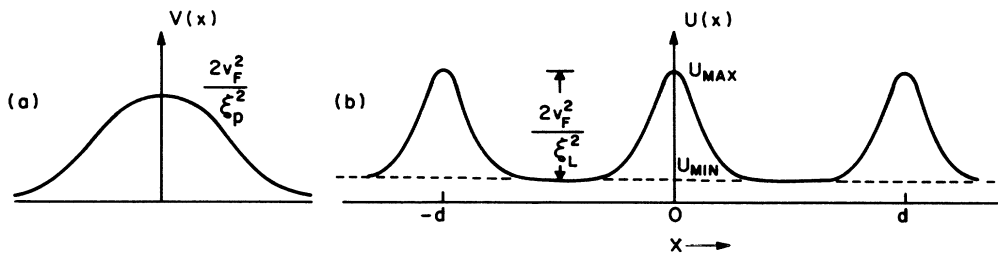


FIG. 1. Schematic structure of (a) single bipolaron potential $u(x)$ and (b) bipolaron lattice potential $u_L(x)$ with periodicity d , where $U_{\max} = (2v_F^2/\xi_L^2)(E'/k^2K')$ and $U_{\min} = (2v_F^2/\xi_L^2)(E'/k^2K' - 1)$.

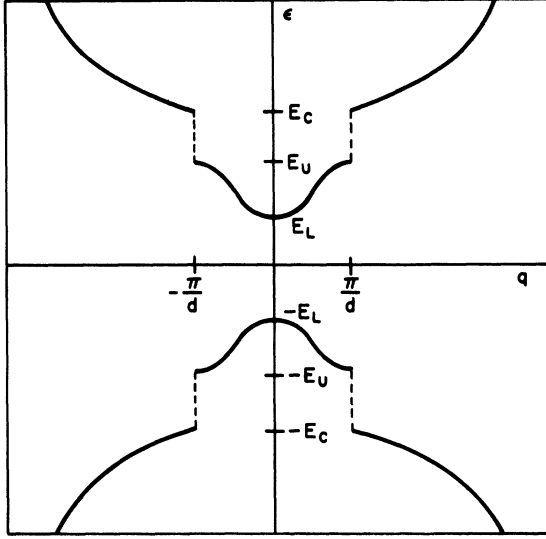


FIG. 2. Energy levels for fermions in a bipolaron lattice in a tetrahedrally bonded homopolymer. The wave vector q is measured from the Fermi wave vector k_F and the energy ϵ from midgap. Note that there are four bands and three gaps present at $q=0, \pm\pi/d$.

$$A = \left[\frac{k^2 \xi_L^2}{v_F^2} \right] (\alpha^2 - \epsilon_q^2) - \frac{2E'}{K'}, \quad \xi = \frac{x}{k \xi_L}. \quad (3.7b)$$

The eigenfunctions $f_q(\zeta)$ and the eigenvalues ϵ_q of the Lamé equation can be obtained using standard methods.^{15,40} Due to the charge conjugation symmetry of the present system the spectrum is symmetric around $\epsilon=0$ and contains four branches (Fig. 2): the valence band, two bipolaron bands symmetrically located about $\epsilon=0$, and a conduction band. There are three gaps in the spectrum. A gap exists between the upper and lower bipolaron bands in the wave-vector range $(-\pi/d < q < \pi/d)$. The other two gaps are at $q = \pm\pi/d$ separating the conduction and upper bipolaron bands for $\epsilon > 0$ and the valence and lower bipolaron bands for $\epsilon < 0$.

The bipolaron bands have eigenvalues $\pm\epsilon_b$ with

$$\epsilon_b^2 = E_U^2 - \left[\frac{v_F k' \text{sn}(\chi, k')}{\xi_L \text{dn}(\chi, k')} \right]^2, \quad (3.8a)$$

where

$$\begin{aligned} E_U^2 &= \alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[1 - \frac{2E'}{K'} \right] \\ &= \epsilon_p^2 + \frac{v_F^2}{k^2 \xi_L^2} \left[\left[\frac{\pi}{2K'} \right]^2 + 1 - \frac{2E'}{K'} \right] \end{aligned} \quad (3.8b)$$

is the upper edge of the bipolaron band and χ is related to the electron momentum q through the parametric equation

$$q_b = \frac{1}{k \xi_L} \left[E(\chi, k') - \chi \left[1 - \frac{E}{K} \right] \right]. \quad (3.9)$$

$E(\chi, k')$ is the incomplete elliptic integral of the second kind. The range $0 < q < \pi/d$ corresponds to $0 < \chi < K'$. Equation (3.8) can also be written as

$$\epsilon_b^2 = E_L^2 + \left[\frac{v_F k' \text{cn}(\chi, k')}{k \xi_L \text{dn}(\chi, k')} \right]^2, \quad (3.10a)$$

where

$$\begin{aligned} E_L^2 &= \alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[k^2 - \frac{2E'}{K'} \right] \\ &= \epsilon_p^2 - \frac{v_F^2}{k^2 \xi_L^2} \left[\frac{2E'}{K'} - k^2 - \left[\frac{\pi}{2K'} \right]^2 \right] \end{aligned} \quad (3.10b)$$

is the lower edge of the bipolaron band. The eigenfunctions in terms of theta functions (θ_i) are

$$f_q^b(x) = C_q \frac{\theta_3 \left[\frac{\pi x}{d} + i \frac{\pi X}{2K} \middle| \tau \right]}{\theta_4 \left[\frac{\pi x}{d} \middle| \tau \right]} e^{iqx}, \quad (3.11)$$

with $\tau = iK'/K$ and C_q is a normalization constant. From (3.11) and the normalization (2.3) one has

$$|f_q^b(x)|^2 = \frac{1}{2L} \frac{\text{dn}^2(\chi, k') - k^2 \text{sn}^2(x/k \xi_L, k)}{\text{dn}^2(\chi, k') - (1 - E/K)}. \quad (3.12)$$

The valence and conduction bands have eigenvalues $\pm\epsilon_c$ with

$$\epsilon_c^2 = E_c^2 + \left[\frac{v_F \text{sn}(\chi, k')}{\xi_L \text{cn}(\chi, k')} \right]^2, \quad (3.13a)$$

where

$$E_c^2 = \alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[1 - \frac{2E'}{K'} + k^2 \right] \quad (3.13b)$$

is the conduction-band edge. χ and q are related by

$$\begin{aligned} q_c - \frac{\pi}{d} &= \frac{1}{k \xi_L} \left[\chi \left[1 - \frac{E}{K} \right] - E(\chi, k') \right. \\ &\quad \left. + \frac{\text{dn}(\chi, k') \text{sn}(\chi, k')}{\text{cn}(\chi, k')} \right]. \end{aligned} \quad (3.14)$$

The range of q is $\pi/d < q < \Lambda$, which corresponds to $0 < \chi < K' - \delta$ with $\delta \rightarrow 0$ as the upper momentum cutoff $\Lambda \rightarrow \infty$. The eigenfunctions are¹⁵

$$f_q^c(x) = C'_q \frac{\theta_4 \left[\frac{\pi x}{d} - i \pi \frac{\chi - K'}{2K} \middle| \tau \right]}{\theta_4 \left[\frac{\pi x}{d} \middle| \tau \right]} e^{iqx}. \quad (3.15)$$

Evaluation of the normalization constant C'_q after some algebra yields

$$|f_q^c(x)|^2 = \frac{1}{2L} \frac{\text{dn}^2(\chi, k') - \text{dn}^2(x/k \xi_L, k) \text{cn}^2(\chi, k')}{\text{dn}^2(\chi, k') - (E/K) \text{cn}^2(\chi, k')}. \quad (3.16)$$

The band edges are related to each other by the following simple relations:

$$E_c^2 = E_U^2 + \left(\frac{v_F}{\xi_L} \right)^2 = E_L^2 + \left(\frac{v_F}{k\xi_L} \right)^2 \quad (3.17a)$$

and

$$E_U^2 = E_L^2 + \left(\frac{k'v_F}{k\xi_L} \right)^2. \quad (3.17b)$$

Furthermore, the moduli k and k' can be expressed in terms of the band edges,

$$k = \left(\frac{E_c^2 - E_U^2}{E_c^2 - E_L^2} \right)^{1/2}, \quad k' = \left(\frac{E_U^2 - E_L^2}{E_c^2 - E_L^2} \right)^{1/2}. \quad (3.18)$$

Next, we check the self-consistency relation explicitly; this will prove the local stability of the solution and will eventually determine ξ_L in terms of ξ_p [Eq. (3.6b)]. Equation (2.9) for a lattice solution should be modified to read as

$$\gamma u_L(x) = \frac{2\gamma^2 a v}{K_0} \sum_q |f_q^b(x)|^2, \quad (3.19)$$

where the summation is over the bipolaron band. Using (3.12) and (3.9) as well as converting the summation into an integral, after changing the integration variable from q to χ one sees that the self-consistency condition is indeed satisfied provided the relation (3.6b) holds.

IV. DENSITY OF STATES AND LOCAL FERMION DENSITY

It is instructive to calculate the electronic density of states of a tetrahedrally bonded polymer system in the presence of a bipolaron lattice. As noted earlier, the density of states is symmetric about the Fermi level and consists of two parts for $\varepsilon > 0$, the upper bipolaron band and the conduction band. In one dimension the density of states is given by

$$n(\varepsilon) = L \left| \frac{dN}{d\varepsilon} \right| = \frac{L}{2\pi} \frac{\left| \frac{dq}{d\chi} \right|}{\left| \frac{d\varepsilon}{d\chi} \right|}. \quad (4.1)$$

For the conduction band we obtain from Eqs. (3.13) and (3.14), after performing algebra,

$$n_c(\varepsilon) = \frac{L}{2\pi} \frac{v_F}{kK\xi_L^4} |\varepsilon| \times \left| \frac{(K-E)v_F^2 + Kk^2\xi_L^2(\varepsilon^2 - E_c^2)}{(\varepsilon^2 - E_c^2)^{1/2}(\varepsilon^2 - E_U^2)^{3/2}(\varepsilon^2 - E_L^2)^{1/2}} \right|. \quad (4.2)$$

Similarly, using Eqs. (3.8) and (3.9) we obtain for the bipolaron band

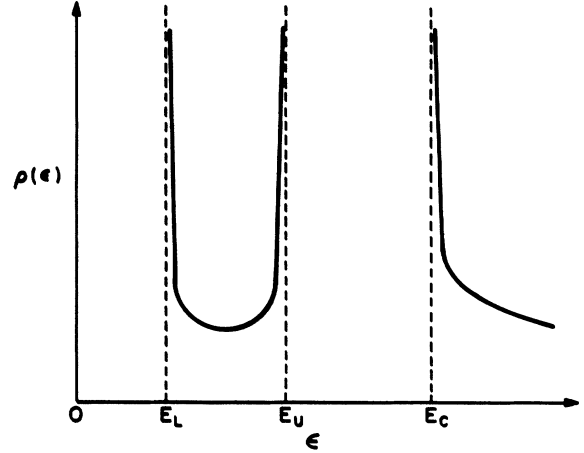


FIG. 3. The electronic density of states of the bipolaron lattice for $\varepsilon > 0$ and an arbitrary bipolaron density ρ_b . The diagram is symmetric about $\varepsilon = 0$.

$$n_b(\varepsilon) = \frac{L}{2\pi} \frac{v_F}{k^2 K \xi_L^2} |\varepsilon| \times \left| \frac{E(E_c^2 - \varepsilon^2) - K(E_U^2 - \varepsilon^2)}{(E_c^2 - \varepsilon^2)^{1/2}(E_U^2 - \varepsilon^2)^{1/2}(E_L^2 - \varepsilon^2)^{1/2}} \right|. \quad (4.3)$$

The density of states is schematically shown in Fig. 3. Its proportionality to the bipolaron density indicates that at very low bipolaron concentration ρ_b is extremely sharp and localized at the single bipolaron level ε_p . With increasing bipolaron concentration the bipolaron band expands while the conduction band shrinks.

Next, we consider the local fermion density which in terms of the original fields is $\sum_n |\Psi_n(x)|^2$, or

$$\rho(x) = \sum_n [|A_n(x)|^2 + |B_n(x)|^2] = \sum_n [|f_n(x-x_0)|^2 + |f_n(x+x_0)|^2]. \quad (4.4)$$

The completeness relation of $(f_n(x-x_0), f_n(x+x_0))$ implies that the sum in (4.4) if taken on all states is x independent. In fact, half of this sum can be subtracted¹⁵ from (4.4) as the background charge. By the charge conjugation symmetry this subtraction is the sum on valence-band states plus one of the bipolaron bands. Hence,

$$\rho(x) = \sum_{\text{bip}} [|f_b(x-x_0)|^2 + |f_b(x+x_0)|^2] = 2 \sum_{\text{bip}} |f_b(x)|^2 + O \left(\frac{x^2 a^2}{\xi_p^4} \right), \quad (4.5)$$

where we have made expansion of $f_b(x \pm x_0)$ to second order. After some algebraic manipulation we obtain

$$\rho(x) = \frac{2\rho_b K v_n}{\pi} [E' - k^2 K' \text{sn}^2(x/k\xi_L, k)]. \quad (4.6)$$

V. ENERGY OF THE BIPOLARON LATTICE

In this section we evaluate the total energy of the bipolaron lattice relative to the bipolaron free ground state,

$$E_{\text{BL}} = E(u_L(x)) - E(u(x)=0), \quad (5.1)$$

where

$$\begin{aligned} \sum_n \varepsilon_n^0 &= -v_n \frac{L}{2\pi} \int_{-\Lambda}^{\Lambda} (\alpha^2 + v_F^2 k^2) dk \\ &= -\frac{v_n L v_F}{2\pi} \left[\Lambda^2 \left[1 + \frac{\alpha^2}{v_F^2 \Lambda^2} \right]^{1/2} + \frac{\alpha^2}{v_F^2} \ln \left[\frac{v_F \Lambda}{\alpha} \left[1 + \left[1 + \frac{\alpha^2}{v_F^2 \Lambda^2} \right]^{1/2} \right] \right] \right]. \end{aligned} \quad (5.3)$$

Next, we calculate the lattice energy. The first term of (5.2) is evaluated using the exact solution (3.6) to give

$$\frac{E^{\text{elast}}}{L} = \frac{K_0}{2\alpha^2 \gamma^2} \left[\frac{v_F^2}{k^2 \xi_L^2} \right]^2 \left[\left[\frac{E'}{K'} \right]^2 + 2 \left[1 - \frac{E}{K} \right] \left[\frac{1}{3}(1+k^2) - \frac{E'}{K'} \right] - \frac{k^2}{3} \right]. \quad (5.4)$$

The second term of (5.2) can be written as

$$\sum_n \varepsilon_n = \sum_n^{\text{upper}} \varepsilon_n + \sum_n^{\text{lower}} \varepsilon_n + \sum_n^{\text{val}} \varepsilon_n. \quad (5.5)$$

The conduction band is empty and the valence band is filled. The bipolaron bands can either be empty or filled depending on p - or n -type doping, respectively. In either case they are symmetrically occupied and therefore do not contribute to (5.5). The sum over the valence band can be evaluated exactly in terms of incomplete elliptic integrals. Using (3.14) and some algebra we finally obtain

$$\frac{E^{\text{elect}}}{L} = -\frac{v_n E_U}{k \pi \xi_L} \left\{ F(\eta, t) \left[k^2 - \left[k'^2 - \frac{E}{K} \right] \left[\frac{1}{k'^2} - \frac{E_c^2}{E_U^2} \right] \right] + \frac{1}{k'^2} \left[k'^2 - \frac{E}{K} \right] E(\eta, t) + \frac{k^2 v_F^2}{E_L^2 \xi_L^2} \Pi(\eta, E_c^2/E_U^2, t) \right\}, \quad (5.6a)$$

where

$$\eta = \sin^{-1} \left[\frac{E_U}{E_c} \text{sn}(K' - \delta, k') \right], \quad t = \frac{k' E_c}{E_U}, \quad (5.6b)$$

and $F(\eta, t)$, $E(\eta, t)$, and $\Pi(\eta, (E_c/E_U)^2, t)$ are the incomplete integrals of the first, second, and third kinds, respectively.

VI. THE DILUTE LIMIT AND THE INTERACTION BETWEEN BIPOLARONS

To extract the nature of bipolaron-bipolaron interaction we need to obtain the energy of the bipolaron lattice in the dilute limit ($k \rightarrow 1$). Expanding to order k'^4 , various band edges [(3.13b), (3.8b), and (3.10b)] behave as

$$E_c^2 = \alpha^2 + \frac{v_F^2}{\xi_p^2} \frac{k'^4}{8}, \quad (6.1)$$

$$E_U^2 = \varepsilon_p^2 + \frac{v_F^2}{\xi_p^2} \left[\frac{k'^2}{2} + \frac{9}{32} k'^4 \right], \quad (6.2)$$

$$E_L^2 = \varepsilon_p^2 - \frac{v_F^2}{\xi_p^2} \left[\frac{k'^2}{2} + \frac{7}{32} k'^4 \right]. \quad (6.3)$$

Note that to $O(k'^2)$ addition of charge to the system symmetrically expands the bipolaron band around the single bipolaron level ε_p (Fig. 4). For low doping (i.e., small number of bipolarons) the electronic energy of the lattice with respect to the ground state can be written as

$$\frac{E^{\text{elect}}}{L\rho_b} = \frac{2\nu_n}{\pi} \left[K \left[1 + \frac{k'^2}{4} + \frac{5}{64}k'^4 \right] \int_0^{\Lambda\xi_p} \left[\alpha^2 + \frac{v_F^2}{\xi_p^2} x^2 \right]^{1/2} dx - k^2 K \int_0^{\text{sn}(K'-\delta, k')/\text{cn}(K'-\delta, k')} \Gamma(x, k') dx + (E - Kk'^2) \int_0^{\text{sn}(K'-\delta, k')/\text{cn}(K'-\delta, k')} \frac{\Gamma(x, k')}{1+x^2} dx \right], \quad (6.4)$$

where

$$\Gamma(x, k') = 1 + A(x)k'^2 + B(x)k'^4, \quad (6.5)$$

$$A(x) = \frac{x^2}{2(1+x^2)} - \frac{v_F^2}{4\xi_p^2} \frac{x^2}{\left[\alpha^2 + \frac{v_F^2}{\xi_p^2} x^2 \right]}, \quad (6.6)$$

$$B(x) = \frac{3}{8} \frac{x^4}{(1+x^2)} + \frac{v_F^2}{64\xi_p^2} \frac{4-5x^2}{\alpha^2 + \frac{v_F^2}{\xi_p^2} x^2} - \frac{v_F^4 x^4}{32\xi_p^4 \left[\alpha^2 + \frac{v_F^2}{\xi_p^2} x^2 \right]^2} - \frac{v_F^2 x^4}{8\xi_p^2 (1+x^2) \left[\alpha^2 + \frac{v_F^2}{\xi_p^2} x^2 \right]}. \quad (6.7)$$

Momentum upper cutoff Λ is related to δ by Eq. (3.14) as

$$k\Lambda\xi_L = \frac{\text{sn}(K'-\delta, k')\text{dn}(K'-\delta, k')}{\text{cn}(K'-\delta, k')}, \quad (6.8)$$

which when expanded to $O(\delta^4)$ yields

$$\Lambda\xi_p = \frac{1}{\delta} \left[1 + \frac{k'^2}{4} + \frac{9}{64}k'^4 \right] \times \left[1 + \left[\frac{E}{K} - \frac{1+k'^2}{3} \right] \delta^2 - \left[\frac{1-k'^2+k^4}{45} \right] \delta^4 \right]. \quad (6.9)$$

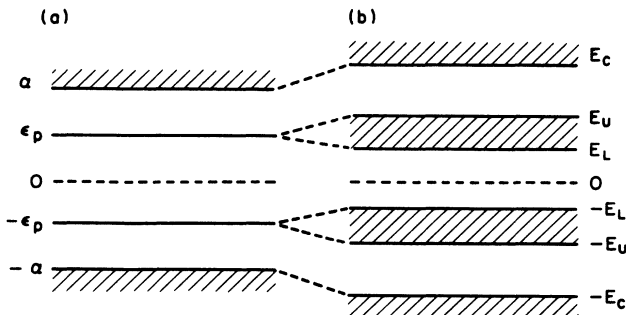


FIG. 4. Schematic band diagrams for (a) a bipolaron and (b) a bipolaron lattice. Note the expansion of the gap and the evolution of bipolaron bands from the localized levels.

Using Eq. (6.9), Eq. (6.4) can be evaluated exactly. When the result is combined with the dilute-limit expansion of the elastic energy (5.4), we obtain

$$\frac{E}{L\rho_b} = \left[\frac{2}{3\alpha} (\alpha^2 - \varepsilon_p^2) + 2\varepsilon_p \right] \left[\left[E - \frac{k'^2}{2} K \right] + \frac{Ek'^2}{4} \right], \quad (6.10)$$

where $\rho_b = 1/d$ is the bipolaron density. The limit $\rho_b \rightarrow 0$ yields the single bipolaron energy with the long-range bipolaron-bipolaron interaction. In this limit $k' \rightarrow 0$ and $2\rho_b\xi_p = [\ln(4/k')]^{-1}$. Expanding E and K in Eq. (6.10) in terms of k'^2 , we find that $O(k'\ln(4/k'))$ and $O(k'^2)$ exactly cancel and to leading order $k'^4 \ln(4/k')$ we obtain

$$\frac{E}{L\rho_b} = E_b \left[1 + 24 \frac{e^{-2/\rho_b\xi_p}}{\rho_b\xi_p} \right]. \quad (6.11)$$

The prefactor in (6.10) and (6.11) is the single bipolaron energy. The second term is a very important result. It represents a repulsive interaction between bipolarons. This interaction is depicted in Fig. 5. It is clear from the figure that the bipolaron lattice is stable in the strict weak-coupling limit ($\Lambda \rightarrow 0$) only up to $\rho_b = \rho^* = 2/\xi_p$. For $\rho > \rho^*$ the system cannot support a lattice; ρ^* minimizes $E/L\rho_b$ and indicates a phase separation of the doped polymer into conducting bipolaron droplets, while the rest of the system is insulating.

The above results must be construed with the caveat that the expansions in terms of k' breakdown for values of ρ close to ρ^* . Furthermore, in actual systems α/Λ is small but finite. Thus, one would expect the value of ρ^* to be reduced for finite Λ due to reduction in phase space.

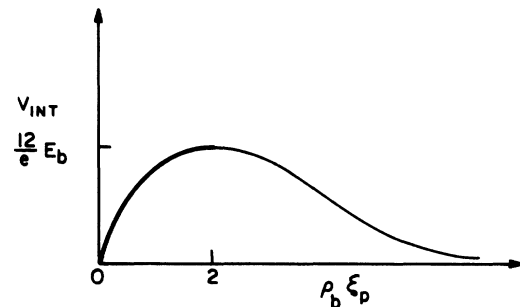


FIG. 5. Repulsive interaction energy of two bipolarons as a function of bipolaron density in dilute bipolaron lattice; $\rho_b\xi_p = 2$ corresponds to the maximum allowed density for which the lattice is stable.

Interaction of bipolarons with dopant ions may also affect ρ^* . Therefore $\rho^* = 2/\xi_p$ as given above only represents a theoretical upper bound on the stability of the bipolaron lattice within the continuum model

The chemical potential for fermions is

$$\mu = \frac{1}{v_n} \frac{\partial E}{\partial \rho_b} = \frac{E_b}{v_n} \left[\left[E - \frac{k'^2}{2} K \right] - \frac{Ek'^2}{4} \right], \quad (6.12)$$

which satisfies $E_U < \mu < E_c$ indicating that the charged bipolaron lattice is energetically the most favorable charged configuration. Therefore, doping (addition or subtraction of charge) proceeds by expanding the bipolaron bands to accommodate precisely all the additional charge rather than adding a fermion to the conduction band or a hole to the bipolaron band.

VII. DISCUSSION AND CONCLUSION

The repulsive interaction between nonlinear excitations or, equivalently, the long-range coherence on the polymer chain manifests itself in the form of superstructures. Therefore, it is instructive to compare the nature of interaction in generically different polymer systems. In the strict weak-coupling limit at very low doping (dilute limit) the interaction between two solitons in degenerate polyenes¹⁵ is purely exponential ($e^{-1/\rho_s \xi}$). The same holds true for the interaction between two bipolarons in nondegenerate polyenes^{9,29} and related polymers ($e^{-2/\rho_b \xi}$). However, in the present system of homopolymers the interaction between two bipolarons is not purely exponential. Instead, as we noted in Sec. VI, it varies with density as $(1/\rho_b) e^{-2/\rho_b \xi}$. This difference may be attributed to the intrinsically different nature of the bonding in the underlying lattice in homopolymers as compared to polyenes. The implications of the above form of repulsive interaction are quite interesting. The soliton lattices (as well as bipolaron lattices) in polyenes are stable for all soliton (bipolaron) densities in the strict weak-coupling limit. On the contrary, the homopolymer system seems to be unable to support a superstructure for an arbitrary density of bipolarons. Instead, the lattice becomes unstable for densities higher than $\rho_b^* = 2/\xi_p$. We note, however, that for finite momentum cutoff, superstructures in polyenes also become unstable at finite densities.^{8,14,15} The effect of finite momentum cutoff in the present system would amount to lowering the value of ρ_b^* . Since the passage from the discrete model to continuum model neglects terms of the order of $(1/\Lambda^2)$, the finite-momentum-cutoff effect must be viewed with caution.

In the present theoretical treatment we have not incorporated a number of physical features. Particularly, the effect of short-range Coulomb interactions,⁴⁴⁻⁴⁷ quantum corrections due to lattice fluctuations,^{48,49} electron-electron correlations, and nonadiabatic phenomena⁵⁰ have been neglected. Furthermore, the role of interchain coupling, side groups, impurities, and disorder have not been considered. In addition, we have not taken into account the finite length^{31,51} of the polymer chain. The adequacy of continuum equations in describing the bipolaron states and superstructures for homopolymers

remains to be investigated. The present analysis can be extended to finite temperatures provided $u(x)$ and ξ_p are replaced by their temperature-dependent terms. Whether periodic superstructures can survive when all the effects mentioned above are taken into account remains an open question.

The theoretical results obtained in this paper can be related to experimental observation of a bipolaron lattice in a homopolymer as follows. First, observe optical absorption in a doped polymer and determine the modulus of the elliptic function k from Eq. (3.18) using the observed values of absorption edges. Note that all the results for the lattice solution are related to single bipolaron parameters through k . Thus, for a given system single bipolaron parameters such as ξ_p are known; the periodicity d , ξ_L , and other parameters associated with the lattice are determined from the knowledge of just one parameter, k . For n -type doping the gaps in the optical-absorption spectrum of a bipolaron lattice are given by

$$E_g^{\text{ib}} = 2E_c = 2 \left[\alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[1 - \frac{2E'}{K'} + k^2 \right] \right]^{1/2} \quad (7.1)$$

for the interband transition,

$$E_g^U = E_c - E_U = \left[\alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[1 - \frac{2E'}{K'} + k^2 \right] \right]^{1/2} - \left[\alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[1 - \frac{2E'}{K'} \right] \right]^{1/2} \quad (7.2)$$

for the transition from the upper bipolaron band to the conduction band, and

$$E_g^L = E_c - (-E_L) = \left[\alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[1 - \frac{2E'}{K'} + k^2 \right] \right]^{1/2} + \left[\alpha^2 + \left[\frac{v_F}{k \xi_L} \right]^2 \left[k^2 - \frac{2E'}{K'} \right] \right]^{1/2} \quad (7.3)$$

for the transition from the lower bipolaron band to the conduction band. Similar transitions arise from the valence band for p -type doping due to the electron-hole symmetry of the one-electron equations (2.2). The sum of these three absorption intensities must satisfy a sum rule³⁹ which is independent of ρ_b . The intraband transitions may be readily observed in polymers such as PDMS. However, for interband transitions, one may have to make recourse to photoinduced absorption.

In conclusion, a simple method to obtain an exact bipolaron lattice solution in the continuum model of tetrahedrally bonded homopolymers and related systems was shown. The low-density limit of the bipolaron lattice energy yields beyond the linear term $E_b \rho_b$ the long-range interaction between bipolarons in the weak-coupling limit. This interaction is repulsive but not purely exponential; instead it varies with bipolaron density as

$(1/\rho_b)\exp(-2/\rho_b\xi_p)$. This imposes an upper limit on $\rho_b = 2/\xi_p$ up to which the bipolaron lattice is stable. The gap $2E_c$ increases with the doping density. It would be worthwhile to observe the details of bipolaron superstructures described in this paper experimentally including the optical absorption. In addition to nondegenerate polyenes, the presence of bipolaron lattices in homopolymers is indicative of a larger class of conducting polymers

which may support periodic superstructures and can be described within the framework of this paper.

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