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LETTER TO THE EDITOR

Non-damping acoustic plasmons in quasi-one-dimensional organic materials

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Abstract. A model potential for some quasi-one-dimensional organic materials is introduced. In this model, electrons are nearly free in the longitudinal direction, but in the transverse direction there are high rectangular periodic barriers which prevent the movement of electrons between adjacent slender fibres. By application of the random phase approximation (RPA), we show that non-damping acoustic plasmons (NDAP), similar to 'slender' acoustic plasmons (SAP) proposed by Y C Lee and co-workers, appear in the system. As an example, we have carried out the calculation on $(TMTSF)_2PF_6$, and are assured of the appearance of NDAP for its electrons under certain conditions. Finally, we show that NDAP play a principal role in the superconductivity of quasi-1D organic materials, and we discuss the conditions that favour the appearance of NDAP.

Recently, a great deal of progress has been made in research in the field of oxide superconductors [1, 2]. However, this type of material is fragile, difficult to shape and unstable and these defects prevent us from making use of them. On the other hand, it is noticeable that all of the oxide superconductors already discovered are quasi-2D; besides, the nearer their structure to a 2D system, the higher their T_c. Thus, it is worth investigating the problem of whether the transition temperatures of quasi-1D superconductors are still higher. In fact, some organic materials are quasi-1D in structure and they are stable and easily shaped. At the end of the last decade, J Ruvalds *et al* [3, 4] showed that if acoustic plasmons exist in a superconductor its transition temperature rises, but in the usual 3D system acoustic plasmons are always damped and so they rarely exist in such a system. In 1983 Y C Lee *et al* [5] showed theoretically that non-Landau damped acoustic plasmons (SAP mode) exist in a slender wire, with radii of only tens of ångströms. However, it is impossible in practice to make such a thin wire artificially. Perhaps in nature such slender materials as quasi-1D organic compounds may exist. In this article we introduce a simple model potential to simulate the quasi-1D structure and apply the RPA to obtain a dielectric function; applying this we show the formation and the existence of NDAP under certain conditions. As an example, we have carried out a numerical calculation on $(TMTSF)_2PF_6$, the result of which implies that NDAP really exist under suitable conditions. Finally, we discuss the conditions favourable to the appearance of NDAP, and propose that the electrons which exchange NDAP will form pairs: the principal source of superconductivity in quasi-1D materials.

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Quasi-1D organic materials behave as metals in the chain direction (defined as longitudinal) on account of their high electric conductivities and compressivity coefficients, but in the transverse direction (perpendicular to the chain) they show characteristics of ionic crystals as their conductivities and compressivity coefficients are much lower [6]. For simplicity, we assume that the lattice is orthorhombic, and take the chain direction to be the Z axis (so that the XY plane is perpendicular to the chain). For simulation, we establish a simple model in which electrons are nearly free along the Z axis (chain direction), but as they move transversally from one chain to the adjacent one they have to penetrate a potential barrier which is anisotropic and periodic in the X and Y directions and is of height U_{0x} or U_{0y} and width S_x or S_y, as shown in figure 1. Writing down the Schrödinger equation for such a system,

$$[-(\hbar^2/2m)\nabla^2 + U(x,y,z)]\Psi(x,y,z) = E\Psi(x,y,z) \tag{1}$$

where

$$U(x,y,z) = U(x) + U(y) + U(z) \qquad U(z) = 0$$

$$U(z) = \begin{cases} 0 & 0 \leqslant x \leqslant r_x \\ U_{0x} & r_x < x \leqslant r_x + s_x \end{cases} \qquad U(y) = \begin{cases} 0 & 0 \leqslant y \leqslant r_y \\ U_{0y} & r_y < y \leqslant r_y + s_y. \end{cases}$$

From (1) we get:

$$[-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2) + U(x)]\Psi(x) = E_x\Psi(x) \tag{1a}$$

$$[-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}y^2) + U(y)]\Psi(y) = E_y\Psi(y) \tag{1b}$$

$$-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}z^2)\Psi(z) = E_z\Psi(z) \tag{1c}$$

$$E_x + E_y + E_z = E. \tag{1d}$$

Solving (1a) under the continuity condition at $x = r_x$, we obtain the permitted range of E_x constrained by

$$|\cos(kr_z)\cosh(k's_z) + [(k'^2 - k^2)/2k'k]\sin(kr_x)\sinh(k's_x)| \leqslant 1 \tag{2}$$

where

$$k^2 = 2mE_x/\hbar^2 \qquad k'^2 = 2m(U_{0x} - E_x)/\hbar^2. \tag{3}$$

Inequality (2) implies that there is an energy band structure in this system, but in the quasi-1D case it is reduced to quasi-energy levels since U_{0x} or s_x is very large and r_x is very small. r_x and s_x can be calculated from the structure of the material and treated as known parameters. Besides, it is reasonable to assume that the ratio of the transverse electric conductivity σ_x to the longitudinal electric conductivity σ_z is equal to the transmission coefficient T†

$$\sigma_x/\sigma_z = T = [16E_x(U_{0x} - E_x)/U_{0x}^2]\exp(-(2s_x/\hbar)\sqrt{2m(U_{0x} - E_x)}). \tag{4}$$

Therefore, the quasi-energy levels E_x and the height of the potential barrier U_{0x} can be solved from (3) and (4), with the values of k and k' limited by (2), in terms of parameters

† See, for example, Schiff [14].

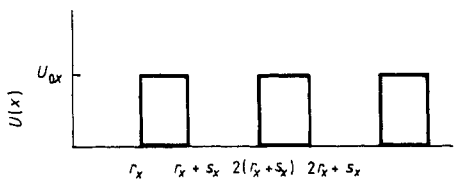

Figure 1. The potential model of quasi-1D organic materials.

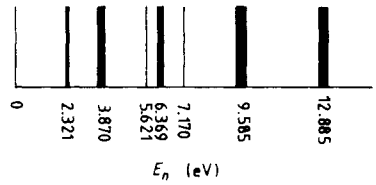

Figure 2. The energy bands of $(TMTSF)_2PF_6$. The quasi-levels appear.

σ_x, σ_z and s_x, which are known from experiment. Similar results are obtained for the Y direction.

As an example, we have carried out the numerical calculation for $(TMTSF)_2PF_6$ from its lattice constant and electric conductivity data (at 300 K) [6]

$a = 7.29$ Å $\quad b = 7.71$ Å $\quad c = 13.52$ Å

$\alpha = 83.39°$ $\quad \beta = 86.27°$ $\quad \gamma = 71.01°$

$\sigma_a = 540\ (\Omega\ \text{cm})^{-1}$ $\quad \sigma_a/\sigma_b = 360$ $\quad \sigma_a/\sigma_c = 30\,000.$

Here, we treat triclinic $(TMTSF)_2PF_6$ as approximately orthorhombic since its lattice angles are near 90°. The a direction should be taken as the Z axis for exceedingly large values of σ_a and then the b and c directions are taken as the X and Y axes respectively. Considering the structure of $(TMTSF)_2PF_6$, we may assume $r_x \simeq s_x$ and $r_y \simeq 3s_y$ for the convenience of computation; then we obtain the following results for the heights of the potential barriers in the X and Y directions: $U_{0x} = 5.104$ eV and $U_{0y} = 9.164$ eV respectively. Energy bands lie between $E_x - \frac{1}{2}\Delta E_x$ and $E_y - \frac{1}{2}\Delta E_y$, and $E_x + \frac{1}{2}\Delta E_x$ and $E_y + \frac{1}{2}\Delta E_y$ respectively, where E_x (eV) = 1.797 or 5.097 and E_y (eV) = 0.524, 2.073, 4.572 or 7.788, and the widths of the bands, ΔE_x (eV) = 0.113 or 0.011 and ΔE_y (eV) = 0.003, 0.021, 0.090 or 0.402, are so narrow that we may consider the energy bands as quasi-energy levels (figure 2). The total transverse energy level is:

$$E_n(\text{eV}) = 2.321 \quad 3.870 \quad 5.621 \quad 6.369 \quad 7.170 \quad 9.585 \quad 12.885$$

$$\Delta E_n(\text{eV}) = 0.116 \quad 0.134 \quad 0.014 \quad 0.203 \quad 0.032 \quad 0.515 \quad 0.413.$$

There is another example: TMTSF–DMTCNQ, for which

$a = 3.938$ Å $\quad b = 8.035$ Å $\quad c = 18.956$ Å

$\alpha = 97.31°$ $\quad \beta = 98.12°$ $\quad \gamma = 91.37°$

$\sigma_a = 600\ (\Omega\ \text{cm})^{-1}$ $\quad \sigma_a/\sigma_b = 300$ $\quad \sigma_a/\sigma_c = 300.$

By calculation we obtain

$$E_n(\text{eV}) = 1.980 \quad 2.627 \quad 3.435$$

$$\Delta E_n(\text{eV}) = 0.067 \quad 0.107 \quad 0.106.$$

We now consider NDAP [7, 8]. The formation and significance of acoustic plasmons (AP) have been discussed by some authors [3, 4], and it is also shown that in 3D systems AP are always damped and so barely exist. However, quasi-1D structures which are the authors' field of study seem to be far more suited to the existence of AP.

In quasi-1D superconductors, on account of the metallic characteristic in their chain direction and high barriers between adjacent chains, the electrons common to all nuclei in a chain (denote their number by N) can be treated as a 1D electron gas, the interactions between chains being neglected. Thus, the Hamiltonian of the system is

$$H = -\sum_{i=1}^{N} \frac{\hbar^2 \nabla_i^2}{2m} + \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + H_+ \tag{5}$$

where the second term is the Coulomb interaction of electrons and the last term is the contribution from the uniformly distributed positive charge background.

In the second quantization, by RPA, we get

$$v(\boldsymbol{q}) \sum_{k} \frac{n_k - n_{k+q}}{\hbar(\omega - \omega_{kq})} = 1 \tag{6}$$

where

$$\hbar\omega_{kq} = (\hbar^2/2m)|\boldsymbol{k}^2 + \boldsymbol{q}^2|^2 - (\hbar^2/2m)k^2 = E_{k+q} - E_k.$$

$\hbar\omega$ is the eigenvalue of energy, n_k, n_{k+q} are Fermi distributions of electrons, and

$$v(\boldsymbol{q}) = \frac{e^2}{AL} \int_A \mathrm{d}^2\boldsymbol{r}' \int_{-\infty}^{+\infty} \mathrm{d}z'' \frac{\mathrm{e}^{\mathrm{i}qz''}}{|(\boldsymbol{r} - \boldsymbol{r}') + z''\hat{z}|}. \tag{7}$$

When the cross section of organic chains (A) is less (or $r_x q$, $r_y q \ll 1$),

$$v(\boldsymbol{q}) \doteq \frac{2e^2}{L} \int_a^{\infty} \frac{\cos(qz'')}{z''} \mathrm{d}z'' = -\frac{2e^2}{L} c_i(qa). \tag{8}$$

Using the linear response theory, we get a dielectric function

$$\varepsilon(\boldsymbol{q}, \omega) = 1 + v(\boldsymbol{q}) \sum_{k} u_k [(E_{k+q} - E_k - (\hbar\omega + \mathrm{i}\eta))^{-1} + (E_{k+q} - E_k + (\hbar\omega + \mathrm{i}\eta))^{-1}] \tag{9}$$

where $\eta = 0^+$.

The form of this $\varepsilon(\boldsymbol{q}, \omega)$ is the same as that in the 3D system. However, the difference lies in $v(\boldsymbol{q})$ in that in our quasi-1D system summation is taken over discrete values of k_x and k_y, but in the general 3D system, k_x, k_y and k_z all vary continuously, and we must replace the summation with an integration.

At low temperatures, we can write approximately:

$$n(E) = \begin{cases} 1 & (E < E_{\mathrm{F}}) \\ 0 & (E > E_{\mathrm{F}}) \end{cases}$$

and get:

$$\varepsilon(\boldsymbol{q}, \omega) = \varepsilon_1 + \mathrm{i}\varepsilon_2 \tag{10}$$

with a real part

$$\varepsilon_1 = 1 - \frac{2ci(qa)}{\pi q a_0} \sum_{E_n < E_{\mathrm{F}}} \ln \left| \frac{s^2 - u_n^{+2}}{s^2 - u_n^{-2}} \right| \tag{10a}$$

and an imaginary part

$$\varepsilon_2 = \begin{cases} \dfrac{-2ci(qa)}{\pi q a_0} \Big| \sum 1 & (\text{where } s \text{ lies between } u_n^+ \text{ and } u_n^-) \\ 0 & (\text{otherwise}) \end{cases} \tag{10b}$$

where $s = \omega/q$, E_{F} is the Fermi energy, a_0 is the Bohr radius, and

$$u_n^{\pm} = u_n \pm \frac{\hbar q}{2m} \qquad u_n = [2(E_F - E_n)/m]^{1/2}.$$

Obviously, $\varepsilon_1 \to \pm\infty$ as $s \to u_n^{+}$. Here s lies between u_n^{+} and u_n^{-} or between u_{n-1}^{-} and u_n^{+}. In the former case there always exists one point mode, $\varepsilon_1 = 0$, $\varepsilon_2 \neq 0$, which corresponds to a damped mode; but in the latter case the mode $\varepsilon_2 = 0$ is undamped. Each damping region is of width $\hbar q/m$. As q becomes sufficiently large the damping regions overlap, so all the AP will be damped, and there exists a maximum of q:

$$q_{\max} = (m/\hbar)\,(u_{n-1,\min} - u_{n,\max})$$

where

$$u_{n,\min} = [2(E_F - E_{n,\max})/m]^{1/2} \qquad u_{n,\max} = [2(E_F - E_{n,\max})/m]^{1/2}.$$

The condition for the existence of AP is $\hbar q/m \ll u_n\,(\Delta u_n = u_{n-1,\min} - u_{n,\max})$. This means that there are two or more transverse quasi-levels below the Fermi energy of the system which must be sufficiently widely separated that each level can house a large number of electrons with different k_z, leading to the collective nature of NDAP.

If the collective oscillation of ions [7] in a real solid is considered, i.e. the action of phonons is taken into account, then the dispersion relation of the electron–phonon system in the zero-temperature limit is:

$$g(\boldsymbol{q}, \omega) = 1 - \frac{\Omega_p^2}{\omega^2} + \frac{2ci(qa)}{\pi q a_0} \sum_{E_n < E_F} \ln \left| \frac{s^2 - u_n^{+2}}{s^2 - u_n^{-2}} \right| \tag{11}$$

where Ω_p is the plasma frequency of the ions when the electrons are treated as a fixed negative background. From this relation we know that if there are NDAP when the action of phonons is not considered, then there are still NDAP when we consider the action of phonons. In short, the condition for the existence of NDAP is that there be two or more transverse quasi-levels sufficiently widely separated below the Fermi energy.

As an example, we have carried out calculations on $(TMTSF)_2PF_6$ and TMTSF–DMTCNQ on the grounds that they exhibit quasi-1D characteristics. If we denote the linear density of the electrons in the system by n_l, then the Fermi energy is

$$E_F = \frac{\pi^2 \hbar^2}{8m} n_l^2. \tag{12}$$

If there are n electrons per cell, then $n_l = n/a$. For $(TMTSF)_2PF_6$, $a = 7.29$ Å, so

$$E_F(n) = \frac{\pi^2 \hbar^2 n^2}{8ma^2} = 0.176n^2(\text{eV}).$$

When $n = 4$, 5 or 6, E_F (eV) = 2.813, 4.395 or 6.329 respectively. From the quasi-level structure mentioned above, we know that NDAP appear only in the case $n \geqslant 5$; but when $n \leqslant 4$, only one level appears in the transverse direction below the Fermi energy and no NDAP exists. However, we can raise E_F by increasing the pressure in the longitudinal direction. For example, if we reduce the lattice constant a of $(TMTSF)_2PF_6$ by 16% to 6.13 Å, then E_F rises to 3.978 eV, and NDAP can exist even when $n = 4$. We get the

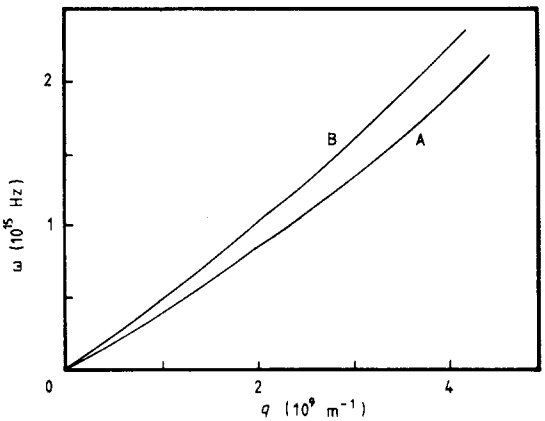

Figure 3. The dispersion curves of NDAP. Curve A is the case in which lattice constant a is reduced to 6.13 Å, $E_F = 3.978$ eV, $E_1 = 2.321 \pm 0.058$ eV, $E_2 = 3.870 \pm 0.067$ eV, $\omega_{NDAP} = 2.02 \times 10^{15}$ Hz, where $q_{max} = 4.35 \times 10^9\ m^{-1}$; curve B is the case in which the structure of $(TMTSF)_2PF_6$ is changed; the leading b direction is the same as the c direction. Where $E_F = 2.813$ eV, $E_1 = 1.048 \pm 0.003$ eV, $E_2 = 2.592 \pm 0.012$ eV, $\omega_{NDAP} = 2.30 \times 10^{15}$ Hz.

dispersion curve shown as curve A in figure 3, $\omega_{NDAP} = 2.02 \times 10^{15}$ Hz as $q_{max} = 4.35 \times 10^9\ m^{-1}$, so the frequency of NDAP is much higher than the Debye frequency of phonons. On the other hand, we can also get two quasi-levels in the transverse direction, below the Fermi energy, by varying the structure of $(TMTSF)_2PF_6$ in the b direction so that it is the same as that in the c direction. The data obtained in this manner for these quasi-levels are

$$E_n(\text{eV}) = 1.048 \quad 2.592 \quad 4.146 \quad 5.096 \quad 6.645$$

$$E_n(\text{eV}) = 0.006 \quad 0.024 \quad 0.042 \quad 0.093 \quad 0.111.$$

There are therefore two transverse levels below $E_F = 2.813$ eV and NDAP exist in the system when $n = 4$. The dispersion curve is shown as curve B in figure 3, $\omega_{NDAP} = 2.30 \times 10^{15}$ Hz as $q_{max} = 4.34 \times 10^9\ m^{-1}$. If the number of conducting electrons in the material is increased still further, we can get NDAP by either of the aforementioned methods.

However, for TMTSF–DMTCNQ, because the value of n is equal to half of that for $(TMTSF)_2PF_6$, the lattice constant in the longitudinal direction is larger than the half value of $(TMTSF)_2PF_6$, and its Fermi energy $E_F = 2.41$ eV is lower than that of $(TMTSF)_2PF_6$. Below this Fermi energy there is only one transverse level, and no NDAP exist in the system.

We have shown that in the simple quasi-1D model, electrons are nearly free in the longitudinal direction but cannot move freely in the transverse direction on account of very high potential barriers, and that energy bands will split into several quasi-energy levels if $\sigma_\parallel$ is much larger than $\sigma_\perp$. Furthermore, we have shown that NDAP appear as the energy band splits into two or more quasi-levels in the transverse direction and that these lie below the Fermi energy. In short, the condition for the existence of NDAP is that there are two or more transverse quasi-levels sufficiently widely separated below the Fermi energy.

The results of research in the field of superconductivity in recent years imply that there is a certain limit of application of traditional BCS theory. Some possible new mechanisms for interpretation of superconductivity have been published [9–12]. The common idea of these theories is that electron (quasi-electron) pair formation is the condition for the appearance of superconductivity. Among a series of proposed mechanisms, special attention was paid to that of the 2D plasmon. In comparison with the original BCS phonon mechanism, the 2D plasmons with a frequency $\omega_P^{(2)} \propto q^{1/2} \sim$ 2500 K mediate the electron–electron attraction. If 2D plasmons actually give rise to the high-T_c superconductivity, would the quasi-1D acoustic plasmon lead to the same? From the last paragraph we know that the frequency of NDAP $\omega_{NDAP} \propto q \sim 15000$ K may mediate the electron–electron attraction by the exchange of NDAP and boost the T_c appreciably. In another case, phonons and NDAP act simultaneously and strengthen the coupling betwen electrons, leading to high-T_c superconductivity. In all cases, high-T_c superconductivity appears if NDAP exist. These NDAP owe their existence to the structure of transverse quasi-levels in the quasi-1D system. They represent the collective oscillation of the electrons in one discrete transverse level against those in an adjacent level. Their analogue in 2D is completely Landau damped.

However, this does not imply that NDAP may exist in all quasi-1D organic conductors even if they have similar characteristics to $(TMTSF)_2PF_6$. For example, the characteristics of TMTSF–DMTCNQ are similar to $(TMTSF)_2PF_6$, but, as mentioned above, there are no NDAP as there is only one transverse quasi-level below the Fermi energy.

In practice we may increase the linear electron density along the longitudinal direction in quasi-1D organic materials by means of raising the pressure in this direction to favour the production of NDAP. But $\omega_{NDAP} \propto q_{max}$ will be low, if the Fermi energy is too high.

The above discussion is not only applicable to organic superconductors, but also to any system in which a metallic characteristic appears in one direction and energy bands split into many quasi-levels in the others. For example, in the case of a strong magnetic field acting in the Z direction, transverse Landau levels may appear in the material, but they are close to each other so a magnetic field of 10^9 T must be imposed, to achieve an energy gap of even 1 meV.

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References

[1] Zhao Zhong-xian *et al* 1987 *Kexue Tongbao* **32** 412
[2] Cava R J *et al* 1987 *Phys. Rev. Lett.* **58** 1676
[3] Ruvalds J 1981 *Adv. Phys.* **30** 677
[4] Tutto I and Ruvalds J 1979 *Phys. Rev.* B **19** 5641
[5] Lee Seulloa Y C and Lee P S 1983 *J. Phys. C: Solid State Phys.* **16** L995–1003
[6] Jerome D and Schulz H J 1982 *Adv. Phys.* **31** 299
[7] Norman W J and March H 1973 *Theoretical Solid State Physics* vol 1 (London: Wiley)
[8] Chock D P and Lee Y C 1970 *Physica* **50** 317
[9] Gu Jianlin *et al* 1987 *Sci. Sinica* A **7** 693
[10] Alexandrov A and Ranninger J 1981 *Phys. Rev.* B **23** 1164

[11] Rice T M and Sueddon L 1981 *Phys. Rev. Lett.* **47** 689
[12] Anderson P W 1987 *Science* **235** 1196
[13] Schrieffer J R 1983 *Theory of Superconductivity*
[14] Schiff L I 1955 *Quantum Mechanics* 2nd edn (New York: Wiley) p 95