

**INTERNATIONAL CENTRE FOR  
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ON THE DIMERIZATION OF LINEAR POLYMERS

C. Aragão de Carvalho



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ON THE DIMERIZATION OF LINEAR POLYMERS \*

C. Aragão de Carvalho \*\*

International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

We use the continuum limit of the Su-Schrieffer-Heeger model for linear polymers to construct its effective potential (Gibbs free energy) both at zero and finite temperature. We study both trans and cis-polymers. Our results show that, depending on a renormalization condition to be extracted from experiment, there are several possibilities for the minima of the dimerized ground state of cis-polymers. All calculations are done in the one-loop approximation.

MIRAMARE - TRIESTE

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\*\* Permanent address: Departamento de Física, Pontifícia Universidade Católica de Rio de Janeiro, C.P. 38071, 22453 Rio de Janeiro RJ, Brazil.

The Su-Schrieffer-Heeger<sup>[1]</sup> model for linear polymers has a Hamiltonian given by

$$H = \sum_n \left\{ \frac{p_n^2}{2M} + \frac{K}{2} (y_{n+1} - y_n)^2 + t_{n+1,n} (c_n c_{n+1}^\dagger + c_{n+1} c_n^\dagger) \right\} \quad (1)$$

$M$  is the mass of the atoms in the linear chain,  $K$  the spring constant for the harmonic potential, the  $y_n$  are displacements of the atoms from their equilibrium positions, the  $c_n^\dagger$  ( $c_n$ ) are creation (annihilation) operators for  $\pi$ -electrons and  $t_{n+1,n}$  is the so-called hopping parameter which we shall take to be:

$$t_{n+1,n} = [t_0 + (-1)^n 2\mu - \gamma(y_{n+1} - y_n)] \quad (2)$$

We have generalized the original model, which had  $\mu = 0$ , to include both trans ( $\mu = 0$ ) and cis ( $\mu \neq 0$ ) polymers.

The model describes the interaction between  $\pi$ -electrons of the atoms of the linear chain and lattice vibrations (phonons) through the electron-phonon coupling built into the last term of the hopping parameter. If one introduces a dimerization parameter  $\varphi_n \equiv (-1)^n y_n$ , one sees that, for  $\mu = 0$ , this coupling is responsible for the nonvanishing expectation value of the dimerization, leading to an alternating structure of double (shorter) and single (larger) bonds. This occurs in the case of trans-polyacetylene, for instance, which is depicted in Figure 1 with its degenerate ground-state. For cis-polymers ( $\mu \neq 0$ ), apart from the dynamical dimerization due to electron-phonon coupling, there is already an extrinsic dimerization due to the alternating hopping. The total dimerization is a combination of the two effects. The example of cis-polyacetylene, illustrated in Figure 2, shows dimerization occurring in both ground and first excited states. We note that in this case the ground state is nondegenerate.

If one is interested in the study of long-range properties of the model it is sometimes useful to go the continuum limit, where the lattice spacing is shrunk to zero. After convenient rescalings of the fields, we end up with a field-theory model describing fermion-boson interactions in 1 + 1 dimensions<sup>[2,3,4]</sup> through a Lagrangean density

$$\mathcal{L} = \left\{ \frac{1}{2m^2} \frac{\partial^2 \varphi}{\partial t^2} - \frac{1}{2} \varphi^2 + \bar{\psi} [i \not{\partial} - \mu - g \varphi] \psi \right\} \quad (3)$$

where  $m$  is a function of  $M$  and  $K$ , whereas  $g$  depends on the electron-phonon coupling  $\gamma$ . The parameter  $\mu$  is the same as in equation (2), thus showing that trans(cis) polymers are described by a Lagrangean with massless (massive) fermions. The partition function (generating functional) for the model is, then, obtained by integrating over the fields. At zero temperature (in Euclidean space) this becomes

$$Z = \int [D\varphi][D\psi][D\psi^+] \exp \{ -S_E[\varphi, \psi, \psi^+, J, \zeta^+, \zeta] \} \quad (4)$$

with  $S_E \equiv \int d^2x_E \mathcal{L}_E$ . The subscript refers to the Euclidean version of the Lagrangean and  $J, \zeta^+, \zeta$  are external fields coupled to  $\varphi, \psi, \psi^+$ , respectively<sup>[6]</sup>.

Since the Lagrangean in (3) is quadratic in either Bose or Fermi fields one might, in principle, integrate over either of them to obtain an effective action for the remaining field. However, the phenomenology of such polymers seems to indicate that the time scale for changes of the bosonic fields (phonons) is much larger than that of the fermionic ones ( $\pi$ -electrons). Thus, it is natural to integrate out the fermions and, furthermore, to perform a semiclassical approximation around STATIC bosonic backgrounds for the effective bosonic theory. This is the so-called adiabatic approximation<sup>[6]</sup>. If, in addition, we only consider saddle-points of the effective action which are constant (independent of space and time) our description amounts to studying the dimerized ground state (as opposed to soliton and polaron ground states<sup>[6,7,8,16]</sup>)

Going through the steps described in the previous paragraph (we set  $\zeta = \zeta^+ = 0$  and expand around constant  $\bar{\varphi}$ ) we obtain, up to one-loop:

$$Z \simeq \exp [ -S_E(\bar{\varphi}, J) ] \det [i \not{\partial} - \mu - g\bar{\varphi}]^2 \det \left[ -\frac{1}{m^2} \frac{\partial^2}{\partial t^2} + 1 \right]^{1/2} \quad (5)$$

(The exponent for the fermion determinant arises because there is a spin index which can be regarded as internal ( $N = 2$ ) symmetry index). The last term is a free-field bosonic contribution which just gives a constant that can be normalized away. If we then take (minus) the logarithm of  $Z$  and Legendre transform (in  $J$ ) we obtain the effective potential  $\Omega$  (or Gibbs free energy per unit of space-time volume):

$$\Omega(\bar{\varphi}) = \frac{1}{2} \bar{\varphi}^2 - 2Tr \ln [i \not{\partial} - \mu - g\bar{\varphi}] \quad (6)$$

The  $Tr$  symbol denotes, in momentum space,  $\int d^2k/(2\pi)^2$  and also a trace over spin indices ( $S_p$ ). Using the two-dimensional property:

$$\det [i \not{\partial} - C] = \det [-\partial^2 + C^2], \quad (7)$$

valid for a constant  $C$ , we may write:

$$\Omega(\bar{\varphi}) = \frac{1}{2} \bar{\varphi}^2 - 2 \int \frac{d^2k}{(2\pi)^2} \ln [k^2 + (\mu + g\bar{\varphi})^2] \quad (8)$$

This expression is clearly divergent and needs to be regularized. Introducing a cutoff  $\Lambda$  such that  $k_1^2 + k_2^2 \leq \Lambda^2$

$$\Omega(\bar{\varphi}) = \frac{1}{2} \bar{\varphi}^2 + \frac{g^2}{2\pi} \left( \bar{\varphi} + \frac{\mu}{g} \right)^2 \left[ \ln \left( \frac{g\bar{\varphi} + \mu}{\Lambda} \right)^2 + 1 \right] \quad (9)$$

Clearly,  $\Omega$  contains terms in  $\bar{\varphi}^2$  and  $\bar{\varphi}$  (the latter being proportional to  $\mu$ ) which are divergent as  $\Lambda \rightarrow \infty$ .

The calculation described above is completely standard in Quantum Field Theory. In fact, it coincides with the calculation of the effective potential for the Gross-Neveu model<sup>[6,9]</sup> in its massive version<sup>[10,11]</sup>. At this point we see that there is a clear difference between the massless (trans) and massive (cis) cases, since the latter yields an additional divergent term in the  $\Lambda \rightarrow \infty$  limit. In Field Theory those divergent (as  $\Lambda \rightarrow \infty$ ) terms are taken care of by introducing counterterms which get rid of the divergent parts. There is an arbitrariness in the way one performs such subtractions which is fixed by imposing one renormalization condition for each subtraction needed. This is a condition on physical parameters which allows one to reexpress the results of calculations in terms of physically measurable quantities. As an example, one could fix the value of the first and second derivatives of the effective potential at an arbitrary renormalization point,  $\varphi_R$ . Then, upon adding the terms  $\frac{1}{2} (Z-1) \bar{\varphi}^2$  and  $(bZ) \bar{\varphi}$  to the effective potential, the values of  $Z$  and  $bZ$  would be fixed by those conditions. In the limit  $\Lambda \rightarrow \infty$ , their infinite parts would cancel those of  $\Omega$  leaving well defined parts. For instance, the conditions:

$$\Omega'_{ren}(\varphi_R) \equiv f(\mu/\varphi_R, g) \varphi_R \quad (10.a)$$

$$\Omega''_{ren}(\varphi_R) \equiv 1, \quad (10.b)$$

where  $f$  is a dimensionless quantity to be fixed by experiment, lead to a potential:

$$\Omega_{ren}(\bar{\varphi}) = \frac{1}{2} (\bar{\varphi}^2 - \varphi_R^2) + h \varphi_R (\bar{\varphi} - \varphi_R) + \frac{g^2}{2\pi} \left( \bar{\varphi} + \frac{\mu}{g} \right)^2 \left[ \ln \left( \frac{\bar{\varphi} + \mu/g}{\varphi_R + \mu/g} \right)^2 \right] - \frac{3g^2}{2\pi} [(\bar{\varphi} + \mu/g)^2 - (\varphi_R + \mu/g)^2] \quad (11.a)$$

$$h(\mu/\varphi_R, g) = - \left[ 1 - \frac{2g}{\pi} \left( \frac{\mu}{\varphi_R} \right) - \frac{2g^2}{\pi} - f \left( \frac{\mu}{\varphi_R}, g \right) \right] \quad (11.b)$$

Note that  $\Omega(\varphi_R) = 0$ .

In Condensed Matter Physics, however, the cutoff  $\Lambda$  has a direct physical interpretation since we are really working with a cutoff theory. In the present case it can be related to the bandwidth for the  $\pi$ -electrons<sup>[6]</sup>. Thus, instead of introducing an arbitrary renormalization point, it is better to perform subtractions at the minimum of the effective potential which is, in fact, the state the system will prefer. Then, it is enough to fix the values of  $Z$  and  $b$  at that point. For example:

$$\Omega'_{ren}(\varphi_m) = 0 \quad (12.a)$$

$$Z(\varphi_m, \mu, g, \Lambda) = 1 \quad (12.b)$$

$$b(\varphi_m, \mu, g, \Lambda) = \bar{b} \quad (12.c)$$

Conditions (12.b) and (12.c) allow one to write both  $\varphi_m$ , the minimum, and  $\mu$  as functions of  $\Lambda$  and  $g$ . In short, both intrinsic ( $\varphi_m$ ) and extrinsic ( $\mu/g$ ) dimerizations are taken as functions of the bandwidth related cutoff,  $\Lambda$ , and the electron-phonon coupling,  $g$ . The total dimerization,  $\phi_m \equiv \varphi_m + (\mu/g)$ , is a function of  $g$  and  $\Lambda$ . We note that this parameter corresponds to the fermion mass divided by  $g$  and is made up of a dynamically generated ( $g\varphi_m$ ) and an explicit ( $\mu$ ) contribution.

The use of (12) on the subtracted potential ( $\Omega \rightarrow \Omega + (Z-1)\bar{\varphi}^2/2 + (bZ)\bar{\varphi}$ ) yields an equation for its extrema:

$$g\phi_m \left[ 1 + \frac{g^2}{\pi} \ln \left( \frac{g^2 \phi_m^2}{\Lambda^2} \right) \right] = \mu - g\bar{b} \quad (13)$$

where  $\phi_m = \varphi_m + (\mu/g)$ . Introducing  $x \equiv g\phi_m/\Lambda$ ,  $\lambda \equiv \pi/2g^2$  and  $a \equiv (\mu - g\bar{b})/\Lambda$ , dimensionless parameters, solutions to (13) can be found graphically ( $x \ln|x| = \lambda[a-x]$ ). If we use the fact that  $\lambda \gg 1$ , the situations that might arise are illustrated in Figure 3. For  $\bar{b} = \mu/g$  we have three solutions corresponding to  $\phi_m = 0, \pm \Lambda e^{-\pi/2g^2}$ . The  $\phi_m = 0$  is a maximum so that we have *degenerate* minima at  $\pm \Lambda e^{-\pi/2g^2}$ . Since for  $\mu = 0$  there would be no need for a  $\bar{\varphi}$  counterterm (i.e.,  $\bar{b} = 0$ ) we see that this reproduces, as  $\mu \rightarrow 0$ , the known results for the trans-polymers: they have a degenerate ground state which corresponds to dimerizations  $\phi_m = \varphi_m = \pm(\Lambda/g) e^{-\pi/2g^2}$ . This is the phenomenon of dynamical mass generation in the massless model. The novelty is that, *even for cis-polymers*, degenerate ground states might occur. That will happen whenever the total dimerization is the same as in the massless theory. We might say that it is as if the intrinsic and extrinsic dimerizations balanced each other. The two other possibilities are  $\bar{b} > \mu/g$  and  $\bar{b} < \mu/g$ . In either case we may have either one ( $\bar{b} \gg \mu/g, \bar{b} \ll \mu/g$ ) or two ( $\bar{b} \sim \mu/g$ ) minima. In the case where two minima occur they will be nondegenerate. Cis-polyacetylene corresponds to Figure (3(b)2), since it is experimentally known that its dimerization parameter (the fermion mass gap divided by  $g$ ) is bigger than the one of trans-polyacetylene. Our analysis seems to show that it is not excluded that we find cis-polymers whose mass gap might be either equal or even smaller than that of its trans-partner. From a theoretical point of view, within the limitations of the model there is nothing to forbid that.

It is very easy to generalize our results to the case where we have a nonzero temperature. That amounts to restricting the Euclidean time,  $\tau$ , to an interval from 0 to  $\beta \equiv 1/kT$  and imposing antiperiodic boundary conditions on fermions and periodic ones on bosons<sup>[12]</sup>. In computing fermionic determinants we have to sum over Matsubara frequencies,  $\omega_n = (2n+1)\pi/\beta$ . The result for the effective potential is just the Gibbs free energy for a Fermi gas whose eigenenergies are those of a Dirac equation for

fermions of mass  $\mu$  in the presence of an external field  $\varphi^{[13]}$ . Since we are dealing with a constant  $\varphi$  we have:

$$\Omega(\beta, \varphi) = \frac{1}{2} \varphi^2 - \frac{4}{\beta} \int \frac{dq}{2\pi} \ell n \cosh \left( \frac{\beta \omega_q}{2} \right) \quad (14)$$

where  $q$  is the spatial component of momentum and  $\omega_q^2 = [q^2 + (\mu + g\varphi)^2]$ . We may separate out the temperature independent part:

$$\Omega(\beta, \varphi) = \frac{1}{2} \varphi^2 - \int \frac{d_q}{\pi} \omega_q - \frac{2}{\beta} \int \frac{dq}{\pi} [\ell n (1 + e^{-\beta \omega_q}) - \ell n 2] \quad (15)$$

The  $T$ -independent term contains the same divergences we find in the zero-temperature theory. One may thus introduce subtractions  $(Z' - 1) \varphi^2/2$  and  $(b' Z') \varphi$  and integrate up to a spatial cutoff  $\Lambda'$  (note that, previously, our cutoff was on the modulus of the two-momentum  $k_\mu$ ; that is why we use primes here). Just as before we may impose renormalization conditions similar to (12) to arrive at:

$$g\phi'_m \left[ 1 - \frac{2g^2}{\pi} \int_0^{\Lambda'} \frac{d_q}{\omega_q} \left( 1 - \frac{2}{1 + e^{\beta \omega_q}} \right) \right] = \mu - b'g \quad (16)$$

It can be easily verified that, apart from the different cutoff, this equation reduces to (13) as  $\beta \rightarrow \infty$ . If we take  $\mu = b' = 0$  we obtain the finite temperature expression for the dimerization (fermion mass) of trans-polymers through the equation:

$$g\phi'_m = \mu + g\varphi'_m = (2\Lambda) \exp \left[ -\frac{\pi}{2g^2} (1 + \alpha(T)) \right] \quad (17.a)$$

$$\alpha(T) = \frac{4g^2}{\pi} \int_0^{\Lambda'} \frac{d_q}{\sqrt{q^2 + g^2 \phi_m'^2}} \cdot \frac{1}{e^{\beta \sqrt{q^2 + g^2 \phi_m'^2}} + 1} \quad (17.b)$$

Since  $\alpha(T)$  is a positive quantity we see that temperature effects tend to decrease the value of the dimerization parameter, thus contributing to close the gap. We note also that  $\alpha(T)$  is finite as  $\Lambda \rightarrow \infty$ . The finite temperature calculation can also be recovered from references [10], [11]. In each case an arbitrary choice of the parameter  $b'$  was made. Such a choice can also be related to a choice of spatial boundary conditions on the field  $\varphi^{[11]}$ .

In conclusion, we have shown that the analysis of cis-polymers requires the introduction of an extra parameter which leads to a new renormalization condition in the field-theoretic treatment. Depending on that condition, different situations might arise with respect to the mass gaps of trans and cis-polymers. In fact one can write a renormalization group equation for the fermionic mass in the (cutoff) form<sup>[14]</sup>:

$$\left[ \Lambda \frac{\partial}{\partial \Lambda} + \tilde{\beta}(g) \frac{\partial}{\partial g} \right] (g\phi'_m) = 0 \quad (18)$$

The different choices of renormalization condition ( $b'$ 's) will be reflected in the different values one obtains for the nonleading contribution to  $\tilde{\beta}^{[11]}$  (the corrections):

$$\tilde{\beta}(g) = -\frac{g^3}{\pi} [1 + \text{corrections}] \quad (19)$$

One has to resort to experimental data (or to calculations outside the scope of the model) to obtain the dependence of, for instance,  $\mu$  on the scale  $\Lambda$  and the electron-phonon coupling  $g$ . That fixes the value of  $b'$  and chooses one of the possibilities depicted in Figure 3 (as in the case of polyacetylene). Alternatively, from a knowledge of the mass gaps of trans and cis-polymers one can deduce which type of potential one is dealing with.

As we completed this work we became aware that the possibility of finding degenerate ground states in cis-polymers has also been considered by Wang, Su and Martins<sup>[15,16]</sup>. We hope, in the near future, to correlate their analysis to the field-theoretic treatment presented here.

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## FIGURE CAPTIONS

Figure 1: Degenerate ground-states (a) and (b) of trans-polyacetylene

Figure 2: The first-excited (c) and the ground-state (d) of cis-polyacetylene

Figure 3a: Graphical solutions of equation (13)

Figure 3b: Types of potential corresponding to each of the solutions in Figure 3(a)

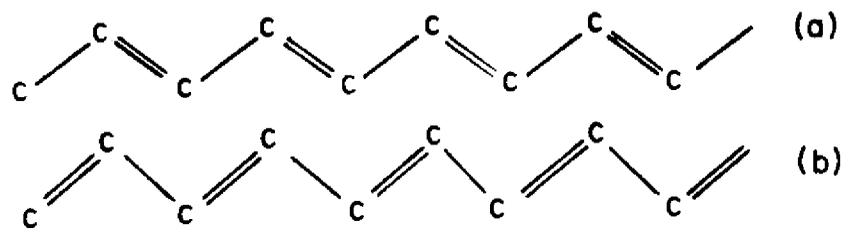


Fig.1

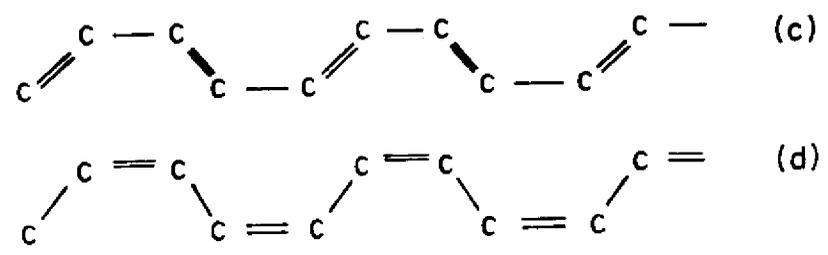


Fig.2

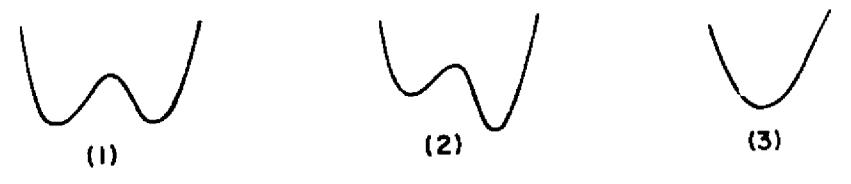


Fig.3a

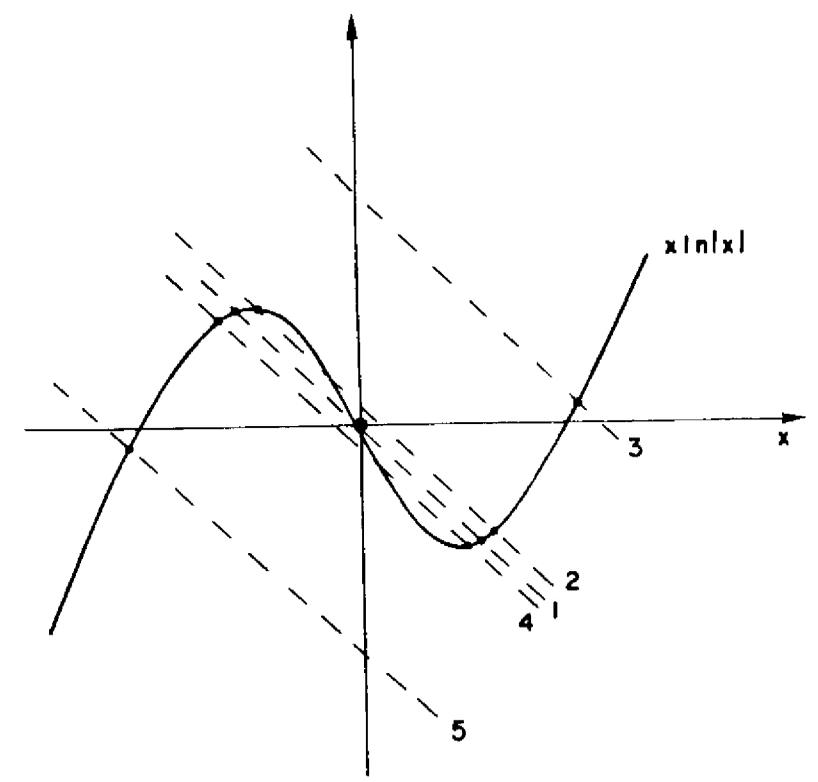
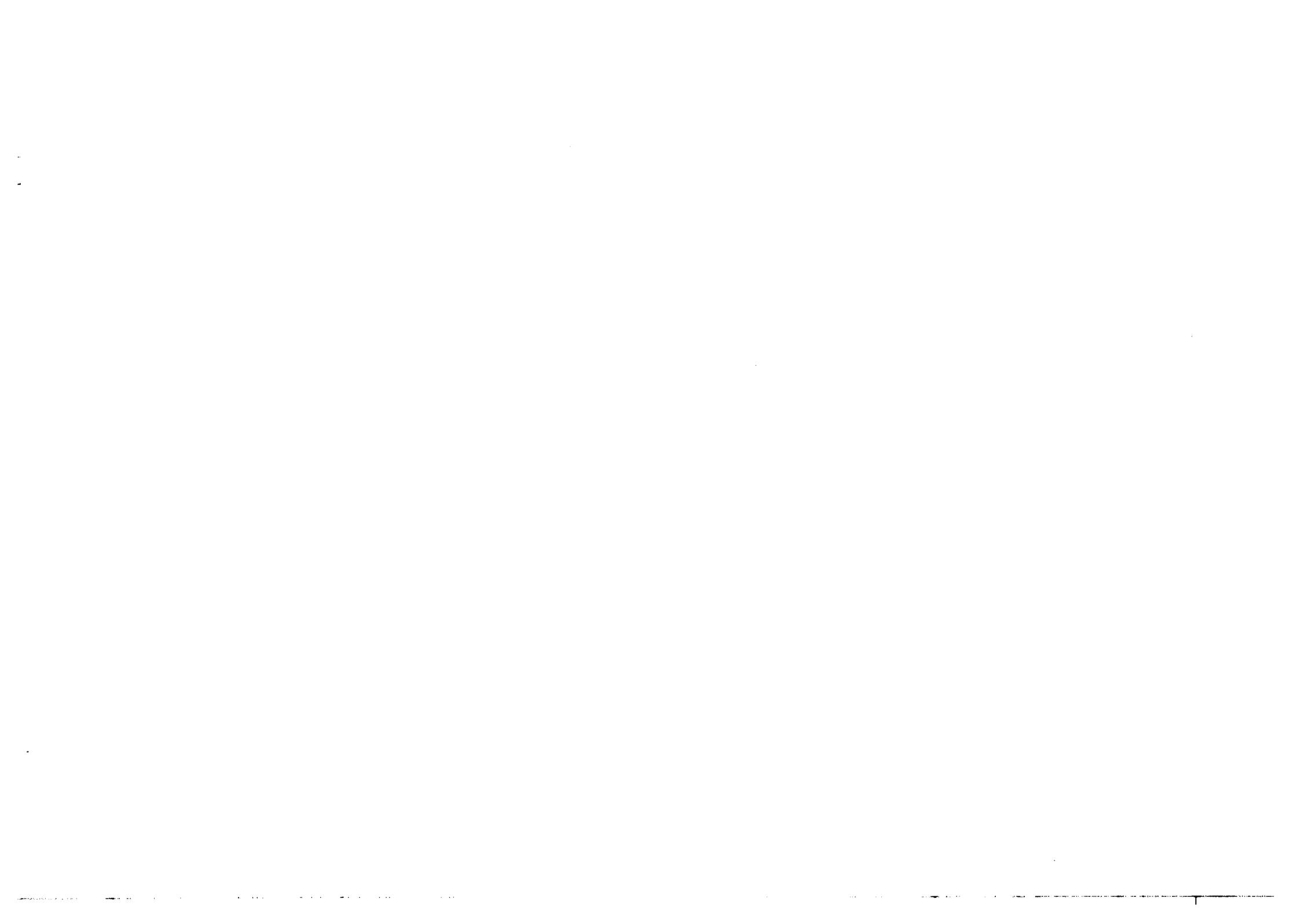


Fig.3b



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