A soliton model for proton conductivity in Langmuir films is presented. The model contains three real scalar fields describing the hydrogen involved in the conduction, the hydrophilic head of the Langmuir film, and the water. Soliton solutions that describe proton motion along the hydrogen bonds are found. Under compression of the film, the distance between the minima of the proton potential and the strength of the hydrogen bonds between the film molecule and the water are changed. Such changes increase the probability of soliton creation. The model presented allows proton conductivity data in Langmuir films to be explained.
— and · · · the covalent and the hydrogen bond, respectively. The simplest example is water \[11\], where \(X\) stands for \(OH\). We can think of one-component and two-component models, but the two-component model is more realistic, because the network is visualized as a diatomic chain, composed of two sublattices, the lighter sublattice describing the protons, and the heavier sublattice the heavier component of the system. Langmuir films are spread and compressed on an aqueous subphase (substrate in our case), and we recall that the experimental measurements in such films are in general done at room temperature. The film is considered an isolated system, having no interference from the water substrate. The water substrate only provides hydration water that participates in the H-bond network. In the model, we do not have to assume any specific crystalline structure for the hydrated water.

The main goal of the present work is to offer a new model to understand the proton conductivity problem in Langmuir films. This model appears through the hydrogen bonds that connect the hydrophilic head of the film molecules to the water, leading to a mechanism that allows the presence of solitons, that drive the proton motion in the network. To do this, we first extend the model of Ref. \[13\] to the case of a three-component chain, which seems to be more appropriate to the investigation of such films. The three-component network in the Langmuir films can be schematically represented by repetitions of \(X - H \cdots Y - H \cdots\). It is composed of protons and the \(X\) and \(Y\) groups that represent \(OH\) and the amphiphilic molecule that characterizes the film, respectively. They are spatially represented in Fig. 1 in the case of the aliphatic acid.

We justify a three-component model for such system recalling that even when one neglects the tail contribution to the motion of the head, it is much heavier than the water counterpart. The proton subchain is much lighter than the other two subchains, so we consider the lighter sublattice coupled with each one of the two other sublattices. We assume the two heavier sublattices do not interact with one another by any other mechanism. That is, the film molecules only interaction with the water is via the hydrogen bonds.

Our model uses three real scalar fields \(\phi, \chi, \psi\), in bidimensional space-time. \(\phi = \phi(x, t)\) describes translational motion of protons, and \(\chi = \chi(x, t)\) and \(\psi = \psi(x, t)\) the motion of \(OH\) groups and amphiphilic molecule subchains, respectively. We use standard notation, with \(x^\alpha = (t, x)\), \(x_{\alpha} = (t, -x)\), and \(\bar{\hbar} = \hbar = c = 1\).

The Lagrangian density is given by

\[
L = \frac{1}{2} \partial_\alpha \phi \partial^\alpha \phi + \frac{1}{2} \mu_1 \partial_\alpha \chi \partial^\alpha \chi + \frac{1}{2} \mu_2 \partial_\alpha \psi \partial^\alpha \psi + \nu_1 \partial_\alpha \phi \partial^\alpha \chi + \nu_2 \partial_\alpha \phi \partial^\alpha \psi - U(\phi, \chi, \psi).
\]

The parameters \(\mu_1, \mu_2, \nu_1, \nu_2\) are real and positive, and \(U = U(\phi, \chi, \psi)\) is the potential. Here we consider the protons as unit mass particles, so the parameters \(\mu_1\) and \(\mu_2\) can represent the mass ratio between the \(OH\) group and the hydrogen, and the amphiphilic molecule and the hydrogen. The other two parameters \(\nu_1\) and \(\nu_2\) describe the derivative coupling between the proton and water and the proton and amphiphilic molecule, respectively.

The equations of motion are

\[
\frac{d^2 \phi}{dx^2} + \nu_1 \frac{d^2 \chi}{dx^2} + \nu_2 \frac{d^2 \psi}{dx^2} = \frac{\partial U}{\partial \phi},
\]

\[
\mu_1 \frac{d^2 \chi}{dx^2} + \nu_1 \frac{d^2 \phi}{dx^2} = \frac{\partial U}{\partial \chi},
\]

and

\[
\mu_2 \frac{d^2 \psi}{dx^2} + \nu_2 \frac{d^2 \phi}{dx^2} = \frac{\partial U}{\partial \psi}.
\]

We consider the case in which the potential is defined by some smooth function \(W = W(\phi, \chi, \psi)\), in the form

\[
U(\phi, \chi, \psi) = \frac{1}{2} W_\phi^2 + \frac{1}{2} W_\chi^2 + \frac{1}{2} W_\psi^2.
\]
$W_\phi$ stands for $\partial W/\partial \phi$, and so forth. This specific form of the potential, together with ideas first introduced in Refs. [15–17] have been recently used to model topological twistons in crystalline polyethylene [18,19]. Other investigations related to the subject can be found in Refs. [20–23] and in references therein.

![Schematic view of the three-component network.](image)

**FIG. 1.** Schematic view of the three-component network. (a) The proton, the $OH$ group, and the head of the film, are represented by small, medium and large circles, respectively. (b) Shows explicitly the atoms of the diagram (a). The hydrophobic tail of the amphiphilic molecule is represented by the gray area.

In Ref. [13] the derivative coupling between the two heavier subchains was considered in the two-component model there studied. In the present work we are considering the three-component model just introduced, and no coupling between the two heavier subchains is taken into account, since they seem to couple mainly through the hydrogen bonds. We follow this reasoning and neglect further couplings between the $\chi$ and $\psi$ fields in the potential. Also the complexity of the problem can be reduced by assuming the heavier subchains contribute insignificantly to the potential, at least when compared to the lighter subchain. Therefore, in this approximation $U = U(\phi)$ depends only on the mobility of the proton field, which yields to

$$U(\phi) = \frac{1}{2} W_\phi^2.$$  \hspace{1cm} (6)

The equations of motion for static field configurations are reduced to

$$\frac{d^2 \phi}{dx^2} + \nu_1 \frac{d^2 \chi}{dx^2} + \nu_2 \frac{d^2 \psi}{dx^2} = W_\phi W_{\phi \phi},$$  \hspace{1cm} (7)
\[ \mu_1 \frac{d^2 \chi}{dx^2} + \nu_1 \frac{d^2 \phi}{dx^2} = 0, \tag{8} \]

and

\[ \mu_2 \frac{d^2 \psi}{dx^2} + \nu_1 \frac{d^2 \phi}{dx^2} = 0. \tag{9} \]

We consider fields whose derivatives present similar asymptotic behavior. In this case the above equations (8) and (9) change to, after setting to zero the integration constants,

\[ \frac{d\chi}{dx} = -\frac{\nu_1}{\mu_1} \frac{d\phi}{dx}, \tag{10} \]

\[ \frac{d\psi}{dx} = -\frac{\nu_2}{\mu_2} \frac{d\phi}{dx}. \tag{11} \]

For static configurations the non-vanishing components of the energy-momentum tensor \( T^{\alpha \beta} \) can be written as

\[ T_{00} = T_g + U(\phi) \] and \( T_{11} = T_g - U(\phi) \), where \( T_g \) represents the gradient contribution. This is given by

\[ T_g = \frac{1}{2} \left[ \left( \frac{d\phi}{dx} \right)^2 + \mu_1 \left( \frac{d\chi}{dx} \right)^2 + \mu_2 \left( \frac{d\psi}{dx} \right)^2 + 2 \nu_1 \left( \frac{d\phi}{dx} \right) \left( \frac{d\chi}{dx} \right) + 2 \nu_2 \left( \frac{d\phi}{dx} \right) \left( \frac{d\psi}{dx} \right) \right]. \tag{12} \]

We use the solutions (10) and (11) to write

\[ T_{00} = \frac{1}{2} \left[ B^2 \left( \frac{d\phi}{dx} \right)^2 + \left( \frac{dW}{d\phi} \right)^2 \right], \tag{13} \]

\[ T_{11} = \frac{1}{2} \left[ B^2 \left( \frac{d\phi}{dx} \right)^2 - \left( \frac{dW}{d\phi} \right)^2 \right], \tag{14} \]

where \( B^2 = 1 - \nu_1^2 / \mu_1 - \nu_2^2 / \mu_2 \). \( B \) is considered real and positive.

The energy density of the static solutions \( \epsilon(x) \) is identified with \( T_{00} \), and it can be written as

\[ \epsilon = \frac{1}{2} \left( B \frac{d\phi}{dx} - W_\phi \right)^2 + B W_\phi \frac{d\phi}{dx}. \tag{15} \]

To minimize the energy, the first term in the above expression is set to zero

\[ \frac{d\phi}{dx} = B^{-1} \frac{dW}{d\phi}, \tag{16} \]

with minimum energy solutions given by

\[ E = B |\Delta W|, \tag{17} \]

where \( \Delta W = W[\phi(\infty)] - W[\phi(-\infty)] \). Solutions to the first-order equation (16) are known as Bogomol’nyi-Prasad-Sommerfeld or BPS solutions \([24,25]\). We notice that \( T_{11} \) vanishes for the BPS solutions, as expected.

For the proton self-interaction we consider

\[ W(\phi) = \frac{1}{3} \lambda \phi^3 - \lambda A^2 \phi, \tag{18} \]
which gives the desirable double-well potential

\[ U(\phi) = \frac{1}{2} \lambda^2 (\phi^2 - A^2)^2, \]  

(19)

where \( A \) is a real and positive dimensionless parameter, \( \lambda \) is also real and has dimension length\(^{-1}\). \( U(\phi) \) has minima located at \( \phi_{\pm} = \pm A \) and the barrier height \( \lambda^2 A^4/2 \). Since the parameter \( A \) gives the minima of the potential, it is directly related to the distance between neighbor oxygens in the film network. This allows the presence of two degenerate ground states, one with all the protons at the position \( A \), and the other with the protons at \(-A\). These two states can be represented by repetitions of the basic entities

\[
\begin{align*}
X - H & \cdots Y - H \cdots \\
X & \cdots H - Y \cdots H -
\end{align*}
\]

The presence of two degenerate minima allows the appearance of solitons, which are extended solutions with finite energy that connect the two degenerate ground states.

To investigate the presence of soliton solutions, we notice that in the present model the first-order equation

\[ \frac{d\phi}{dx} = \lambda B^{-1} (\phi^2 - A^2), \]  

(20)

It is solved to give the kink solutions

\[ \phi(x) = A \tanh \left( AB^{-1} \bar{x} \right). \]  

(21)

Here \( \bar{x} \) stands for \( \lambda x \), and is dimensionless. The parameters \( A \) and \( B \) determine the energy \( (4/3)A^3 B^{-1} \), and the width \( l \sim B/A \) of the soliton solutions. \( A \) is related to the distance between neighbor oxygens in the H-bond network. It is an important parameter because under compression, conductivity and surface potential of the film change significantly when the critical area per head group limit is reached \[1–7\]. \( B \) is an effective parameter, that depends on the fundamental parameters \( \mu_1, \mu_2, \nu_1, \nu_2 \) in a specific way, imposed by the field-theoretical model here considered. Although our model is microscopic, we can think of \( B \) as a phenomenological parameter, used to infer the width and the energy of the soliton solutions. The soliton solutions spring in response to nonlinear effects, and describe proton mobility in the network. The above solutions show that protons migrate from \( A \) to \(-A\), but this migration takes several units in the chain network, given in accordance with the width \( l \sim B/A \) of the solution. The main characteristics of the solution is illustrated in Fig. 2, where the soliton and the asymptotic values in the chain network is depicted. Evidently, under the presence of an external electric field the soliton may move, giving rise to a steady current along the direction dictated by the external electric field. The picture is similar to that in the original work on solitons in hydrogen-bonded network \[1-3\].

We consider a spatial arrangement of the molecules as in Ref. \[10\]. As the film is compressed, the area per amphiphilic unit reaches a critical limit, in which the distance between two consecutive COOH groups is around 7 Å; see Fig. 1. At this point, the oxygens from the OH and film head groups are about 2.4 Å apart. The hydrogen bonds get stronger, bridging the water to the film head tightly, which forms the network that allows the proton conduction. Experimental data shows that the conductivity increases with decreasing of film area. This aspect can be incorporated in the model if we assume the energy of the kink decreases with area per amphiphilic molecule. We do this by requiring the parameter \( A \) to decrease with the distance between the head groups.
When $A$ decreases, the parameters $\nu_1$ and $\nu_2$ that control the derivative coupling should increase, because when the head of the amphiphilic molecule gets closer to the water molecule, the derivative coupling should become more effective. Since $B$ is given by $B = 1 - \frac{\nu_1^2}{\mu_1} - \frac{\nu_2^2}{\mu_2}$, for increasing $\nu_1$ and $\nu_2$, it should consequently decrease. Although we do not know the exact way $B$ decreases, we can compare it with $A$. We can consider, for instance, the simplest possibility in which the ratio $A/B$ remains constant. This approximation introduces two important consequences: i) the soliton width depends on $A/B$, so it should not depend on the film compression; ii) the energy of the soliton depends on $A^3/B$, so it should only depend on $A^2$. With this assumption, our model predicts that the energy of the soliton should vary at the rate $E/E_0 = A^2/A_0^2$, for some reference value $A_0$. As the energy is reduced, the probability of soliton creation is increased, yielding a higher proton conductivity in agreement with the experimental results. In summary, the formalism presented here allows proton conductivity data in Langmuir films to be explained. Because the physical grounds have been established, one can now extend the soliton model to treat the data quantitatively, which will be the subject of our further investigation. In addition, the framework may be applied to proton conductance in more involved systems such as cell membranes, where proton conductance
is believed to play an important role \[1\]. Also it may be useful in the attempts to investigate effects from alcohols on lateral conductance \[26\].

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