DNA Plasmon

L. L. Van Zandt and V. K. Saxena
Department of Physics, Purdue University, West Lafayette, Indiana 47907

(Received 25 April 1988)

As a consequence of the charged nature of a dissolved DNA polymer and its sheath of counterions we predict that there should exist normal modes of the system characterized by substantial longitudinal electric fields and relatively small motion of the atoms and ions. This longitudinal phonon is the one-dimensional counterpart of the plasmon excitation of three-dimensional conductors, and of the surface plasmon of two-dimensional charged systems. The frequency of the DNA plasmon, as a function of excitation wavelength, is linear in inverse wavelength at long wavelengths.

PACS numbers: 87.15.Mi, 33.20.Bx, 68.45.Kg

In three-dimensional systems containing mobile charge carriers such as free electrons, holes, or ions, longitudinal density oscillations coupled with longitudinal electric fields are a well-known feature of the spectrum of elementary oscillations. These "plasmons" have frequencies nearly independent of their wavelength, proportional to q^0. In the case of good metals, they lie in the uv spectral range. A similar phenomenon is well known in two-dimensional conducting systems as, for example, at a plane surface of a metal. Charge-density oscillations confined to the surface and accompanying electromagnetic fields essentially localized at the surface —surface plasmons—have frequencies near 71% of the three-dimensional or bulk plasmons of the same material. In the long-wavelength limit, however, some types of these oscillations have their frequencies proportional to $q^{1/2}$. We study here a one-dimensional charged system, dissolved DNA polymer, and find a wavelength dependence of q^1 for the analogous modes.

Our one-dimensional system is DNA long-chain polymer dissolved in aqueous medium, typically a few millimolar saline. This system differs from its higher-dimensional, metallic analogs in several interesting respects: First, two species of charge carrier are involved in the motion, the negatively charged polymer chain and the predominantly positively charged counterions in the nearby water. The much greater mass of the charge carriers of this molecular system compared to electronic carriers moves the characteristic frequencies of all phenomena to correspondingly lower values. Second, the non-Coulombic forces between the system components, the atomic elasticities, play a much greater role in this system than in the metallic cases.

We consider a wave of electromagnetic-elastic disturbance propagating down a long chain. When electric forces are accounted for simply as long-range atom-to-atom force constants, the atomic equations of motion take the form[1]

$$m_i \ddot{r}_i = \sum_j D_{ij} \delta r_j. \tag{1}$$

(Exactly how these force constants are modeled makes some numerical differences in the results without changing the essential features. We are currently developing an improved version of the intra-base-pair force model which in preliminary results has dropped the plasmon velocity to 20 km/sec. This is still 10 times the sound speed.)

An additional degree of freedom $s(z)$ describes the displacement of the first hydration layer containing the counterions.[2] Its elastic properties and inertia are taken to be those of ordinary water, and its equation of motion that of a simple sound wave. When long-range couplings are treated with an explicit electric field, the right-hand side of (1) acquires another term (with a corresponding reduction in the range of j summation):

$$\sum_j D_{ij} \delta r_j - \gamma_i \dot{s}(z) + E_z(r_i) e_i. \tag{2}$$

The e_i are the partial charges on the atoms and $\mathbf{E}(r_i)$ is the electric field at atom i. We have also added a term describing the polymer to hydration sheath coupling which includes the damping effects. (See also Davis and Van Zandt.[2])

To evaluate **E**, Gauss' law is used to relate **E** and the electric polarization **P**. The polarization is in turn written in terms of the atomic displacements and the partial charges,

$$P = \left[\sum_i \delta r_i e_i - \lambda s(z) \right] \Big/ \pi r_1^2 a. \tag{3}$$

The linear charge density of the molecule is λ, and hence that for the hydration layer is $-\lambda$.

The tangential **E** field is made continuous across the boundary between the hydration layer and the bulk solvent. The normal **D** field is discontinuous in the amount of a surface charge layer whose magnitude is found from the ion current density in the solvent as determined from E_n and solvent conductivity σ. Standard manipulation of Maxwell's equations followed by Fourier expansion of **E** in $e^{iqz - i\omega t}$ yields a Bessel equation for E_z and another for E_r. For the truly one-dimensional system, one polymer molecule in an ocean of solvent, the appropriate choice of solutions are Hankel functions of the second kind. (Fitting fields to close lying neighbors in a denser solution would require a modified choice, of course, and appropriately change the functional form of the result; the problem would no longer be one dimensional.)

We apply the boundary conditions to obtain the field at the molecule (the necessary formalism is inappropriate to a Letter; the details are being published elsewhere):

$$E_z(\omega)=\frac{P(\omega)qvH_0(\kappa r_1)}{(i\sigma+\epsilon_{\text{out}}qv)2H_1(\kappa r_1)/\epsilon_{\text{in}}\kappa r_1-H_0(\kappa r_1)qv}. \tag{4}$$

In this expression σ is the conductivity of the saline medium, ϵ_{in} and ϵ_{out} are the dielectric constants of the hydrated molecular core and the surrounding medium, respectively, v is the velocity of the traveling disturbance $v=\omega/q$, and

$$\kappa^2=q^2(1-\mu_0\epsilon_{\text{out}}v^2+i\mu_0\sigma v/q). \tag{5}$$

We can obtain a simple form for E_z in the small-q limit of all these expressions:

$$E_z=P\mu_0v^2q^2r_1^2\ln\{r_1[\sigma\mu_0vq]^{1/2}\}. \tag{6}$$

We see that the effect of this form for E_z is to add force terms in the equation of motion, Eq. (2), proportional to q^2. The second time derivative in the inertial term carries a factor ω^2, and hence $\omega=v_pq$. The factor $q^{1/2}$ within the logarithm can be separated as a separate term in $\ln(q^{1/2})$ giving a very weak singularity at very small q.

Figure 1 shows a more complete solution of the normal mode problem arising from the equation of motion (2). We can see in this both the ordinary acoustic-phonon branches as we have discussed elsewhere, along with a few of the lowest optical branches, and the plasmon branch which is the point at issue here.

Damping terms describing a mixed viscoelastic coupling between the central polymer core and the solvent hydration shell together with a viscous damping between the hydration shell and the outer bulk water were included in the equations of motion. These terms not only increase the verisimilitude of the calculation but also enable us to evaluate the associated linewidths. There is some contention in the experimental literature[3] over the question of whether the ordinary acoustic vibration modes are or are not overdamped. We have chosen values of the damping coefficients that cause definite overdamping of the acoustic modes.[4] While the resulting Q values ($Q=\omega/\Delta\omega$) obtained for all the oscillations are frequency and wavelength dependent, for a typical value of q we obtain $Q=0.2$ for the acoustic phonons and $Q=4.8$ for the plasmons. The microwave acoustic phonons are overdamped in this calculation while the plasmons are well defined. The reason for the difference between the damping behavior of these two different normal modes lies first in the higher frequency of the plasmons relative to the phonons, and second in the relatively smaller amplitude of the motions of the atoms in the plasmon. Essentially the phonons are mechanical vibrations and the plasmon is more electrical in character.

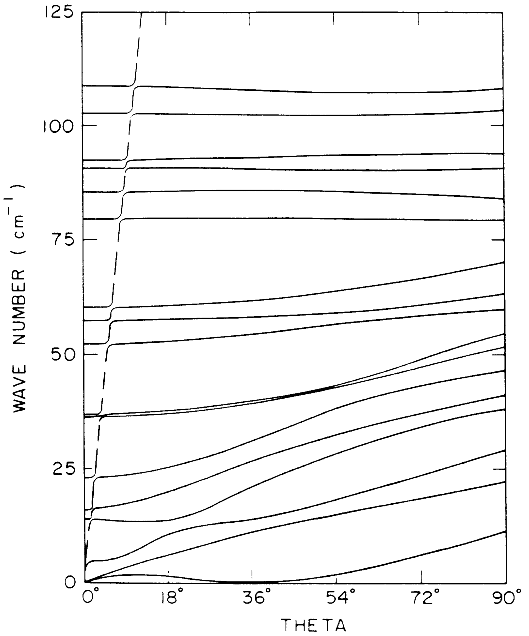

FIG. 1. Excitation spectrum of DNA—poly dG : poly dc—in the lower-frequency range. The lowest-lying phonon branch is torsional in character around the origin, and describes bending where it returns to zero frequency around $\vartheta=36°$. The second branch up is the compressional-wave acoustic spectrum. Several optical branches are shown, but by no means the complete spectrum. The most steeply sloping acoustic branch, drawn with the broken line is the DNA plasmon.

We do not expect the observation and identification of the DNA plasmon to be easy. One favorable feature of the excitation, for observational purposes, is the large electric dipole moment associated with it. An unfavorable circumstance is that the plasmon is a property of dissolved material. The random orientations of dissolved molecules eliminate the q selection that is so useful in spectroscopy on crystalline or partially ordered material; if the material is sufficiently concentrated to be orientable, the one-dimensional nature of the phenomenon—and its signature, the linear $\omega(q)$—is lost.

Finally, the high velocity of the waves causes experimental problems. Acoustic waves (if not overdamped) are expected on uniform-length, plasmid-derived material in the frequency range 2 to 20 GHz.[5] Plasmons, having a wave velocity 20 times higher, are to be expected in the 40- to 400-GHz (or higher) range. This range of frequencies is awkwardly high for current microwave technology, although the free-electron laser may ultimately be useful in this regard. The frequency range is rather too low, however, for long-wavelength optical spectroscopy. Despite these difficulties, we believe the predicted low damping and strong electromagnetic coupling offer reasonable hope for observing a most interesting new phenomenon.

This work was supported by ONR Contract No. N00014-87-K-0162 funded by the Strategic Defense Initiative Organization.

---

[1] E.g., R. E. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, London, 1955), Sect. 1.6. In the Purdue group we have been applying this approach to DNA polymer in a series of publications for some years now beginning with J. M. Eyster and E. W. Prohofsky, Biopolymers **13**, 2505 (1974).

[2] Almost all the counterions, >90%, are contained within the first 5 Å of solvent out from the polymer "surface," the so-called Manning condensation layer; over 80% are within the first 3.1 Å, one monolayer of water out. This is virtually independent of the distant solvent ion concentration. The remaining 5%–10% of ions necessary for total charge neutrality dribble off in a Debye-Huckel–type exponential tail. This behavior is calculated with a Monte Carlo approach by Le Brett and B. Zimm, Biopolymers **23**, 271 (1984); a numerical solution of the Poisson-Boltzmann equations showing practically indistinguishable results from Le Brett and Zimm, as well as including a detailed exposition of the sheath model invoked here, is available in M. E. Davis and L. L. Van Zandt, Phys. Rev. **37**, 888 (1988). The farther out from the polymer core an ion lies and hence the closer the intervening compensating charge fraction is to unity, the less important dynamically the ion becomes. Hence we have taken one water layer thickness to define our hydration water-counterion sheath. Varying this thickness parameter in the calculations makes unimportant changes.

[3] C. Gabriel, E. H. Grant, R. Tata, P. R. Brown, B. Gestblom, and E. Noreland, Nature (London) **328**, 145 (1987).

[4] N. J. Tao, S. M. Lindsay, and A. Rupprecht, Biopolymers **26**, 171 (1987).

[5] G. S. Edwards, C. C. Davis, J. D. Saffer, and M. L. Swicord, Phys. Rev. Lett. **53**, 1284 (1984).