$T > T_m$ there is no hysteresis in the conductivity-temperature curves, and $\sigma_{\parallel}(T)$ obeys the relationship (*1, 3, 15, 16*)

$$1/\sigma_{\parallel}(T) = a + bT^{\gamma} \quad (2)$$

where a and b are constants. For all crystals examined, a least-squares fitting to Eq. 2 yields $\gamma = 1.9 \pm 0.1$, and a plot of $\log\{1 - [\sigma(295°K)/\sigma(T)]\}$ versus T yields a superimposable family of curves; this result has been shown to provide assurance of the reliability of the measurements and of a well-defined scattering mechanism (*15*). The value of γ obtained is distinctly different from the value $\gamma = 1$ found for simple metals and is similar to that found for several other molecular metals, 2.0 to 2.4 (*15, 16*).

Upon cooling below T_m the conductivity abruptly decreases and then continues to slowly decrease with further cooling (Fig. 2). This behavior suggests that a Peierls transition (*1-4*) or a first-order phase transition is taking place. Raman spectral studies down to 4°K do indicate that the lattice charge distribution, that is, the average degree of partial oxidation of NiPc, remains unaltered through this transition. Pronounced hysteresis in d-c conductivity observed upon passage through T_m is suggestive of contributions from stress at the contacts, and microwave conductivity studies in collaboration with T. Poehler suggest that the transition occurs at lower temperatures in unstressed crystals.

Thus, the temperature dependence of the conductivity of $NiPcI_{1.0}$ is metal-like, and the mean free path at room temperature compares favorably with that of the most highly conductive materials composed of molecular stacks. This study and related work (*8*) confirm the idea that the partial oxidation of metallomacrocyclic systems is a chemically versatile synthetic route to a wide array of new molecular metals.

C. J. SCHRAMM, D. R. STOJAKOVIC
B. M. HOFFMAN, T. J. MARKS
Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201

References and Notes

1. H. J. Keller, Ed., *Chemistry and Physics of One-Dimensional Metals* (Plenum, New York, 1977).
2. J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.* **20**, 1 (1976).
3. A. J. Berlinsky, *Contemp. Phys.* **17**, 331 (1976).
4. Z. G. Soos and D. J. Klein, in *Molecular Associations*, R. Foster, Ed. (Academic Press, New York, 1975), chap. 1; W. D. Metz, *Science* **190**, 450 (1975).
5. J. L. Peterson, C. J. Schramm, B. M. Hoffman, T. J. Marks, *J. Am. Chem. Soc.* **99**, 286 (1977).
6. T. J. Marks, *Ann. N.Y. Acad. Sci.*, in press.
7. A. Gleizes, T. J. Marks, J. A. Ibers, *J. Am. Chem. Soc.* **97**, 3545 (1975); M. A. Cowie *et al.*, in preparation; T. J. Marks *et al.*, *J. Chem. Soc. Chem. Commun.* **1976**, 444 (1976).
8. T. E. Phillips and B. M. Hoffman, *J. Am. Chem. Soc.* **99**, 7734 (1977).
9. T. E. Phillips, R. P. Scaringe, B. M. Hoffman, J. A. Ibers, in preparation.
10. C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, T. J. Marks, J. A. Ibers, in preparation.
11. D. W. Kalina, D. R. Stojakovic, R. C. Teitelbaum, T. J. Marks, in preparation.
12. T. E. Phillips, J. R. Anderson, B. M. Hoffman, in preparation. Measurements were made with the precautions suggested by D. E. Schafer, F. Wudl, G. A. Thomas, J. P. Ferraris, and D. O. Cowan [*Solid State Commun.* **14**, 347 (1974)].
13. G. A. Thomas *et al.*, *Phys. Rev. Sect. B* **13**, 5105 (1976).
14. N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1971).
15. L. C. Isett and E. A. Perez-Albuerne, *Solid State Commun.* **21**, 433 (1977).
16. A. N. Bloch, D. O. Cowan, K. Beckgaard, R. E. Pyle, R. H. Bands, T. O. Poehler, *Phys. Rev. Lett.* **34**, 1561 (1975).
17. V. Walatka, Jr., and J. H. Perlstein, *Mol. Cryst. Liq. Cryst.* **15**, 269 (1971).
18. *CRC Handbook of Chemistry and Physics* (CRC Press, Cleveland, ed. 58, 1977), p. F-170.
19. This research was supported by grants from the Northwestern Materials Research Center (NSF DMR 72-0319AO6), the Paint Research Institute (53 Co to T.J.M.), and the U.S. Office of Naval Research (to T.J.M.). T.J.M. is a Camille and Henry Dreyfus Foundation teacher-scholar.

26 August 1977; revised 20 December 1977

Periodicity and Chaos in Coupled Nonlinear Oscillators

Abstract. *A system of coupled tunnel diode relaxation oscillators shows a variety of complex periodic states as the external voltage is varied. The existence of chaotic or nonperiodic states is more dependent on the nature of the coupling than on the number of degrees of freedom. A simple but accurate numerical model shows many of the phenomena observed experimentally.*

Nonlinear models of physical and biological systems sometimes show nonperiodic time evolution even though they involve only a few degrees of freedom (dynamical variables) (*1*). This phenomenon has been noted in models of fluid motion (*2*), populations (*3*), physiological control systems (*4*), ion motion in electric and magnetic fields (*5*), and geomagnetism (*6*). A number of investigators have suggested that the onset of turbulence in fluids and the behavior of other complicated systems might be understandable in terms of models having far fewer variables than the systems they represent (*7*). However, this hypothesis has proved exceedingly hard to test because of the difficulty of using experimental data to generate or test models in systems with many degrees of freedom. In response to a suggestion by R. Landauer, we have studied a system of coupled electronic relaxation oscillators (*8*) which has particular advantages for efforts to understand the conditions under which a dissipative dynamical system can exhibit nonperiodic behavior.

For a certain type of coupling (see below), we find experimentally that a two- or three-oscillator system frequently has an apparently erratic time dependence. However, phase space diagrams and high-resolution frequency spectra of the diode voltages show convincingly that there is usually a single time (often quite long as compared to the natural frequencies of oscillation) over which the oscillators are periodic. We observe numerous transitions between different dynamical regimes as the (time-independent) applied voltage is varied. Using a simple mathematical model of the experiment, we have made accurate numerical computations which are in agreement with these experimental observations. Furthermore, a second coupling scheme transforms the system into one that does show regimes with intrinsic broadband noise and trajectories uniformly filling a region of the phase space.

The systems we have studied consist of tunnel diode relaxation oscillators which are resistively coupled, as shown in Fig. 1A. The tunnel diodes (TD_1 and TD_2) (1N3720) are hysteretic devices with the following properties. As the diode current increases, the voltage across it remains low (less than 0.15 V) until the current exceeds 22 mA, when the voltage rises suddenly to about 0.55 V. If the current now declines, the voltage hardly changes until the current reaches 3 mA, at which point the voltage drops essentially to zero. A tunnel diode in series with a d-c voltage source and inductor will oscillate spontaneously if the d-c load line intersects only the negative resistance region of the current-voltage characteristic. The frequency of oscillation is determined roughly by the ratio of resistance to inductance of the circuit. The voltage wave form is essentially rectangular (Fig. 1B), whereas the current is composed of exponential curves.

Several of these oscillators, with different natural frequencies, may be coupled together in different ways. The resistor R (Fig. 1A) provides such a coupling, because the voltage applied to one oscillator depends on the current being drawn by the others. Alternately (or in addition), a cross resistor R_c joining the two diodes directly may be used. In this case the current through a diode depends not only on the current through its inductor but also on the relative values of the voltages V_1 and V_2.

We begin by describing the behavior of a two-oscillator system when R_c is infinite. Basically we find that all four dynamical variables (the two diode voltages V_1 and V_2 and the corresponding currents I_1 and I_2) are strictly periodic with period T for all applied voltages at which oscillation occurs. The two oscillators synchronize in such a way that m cycles of one and n cycles of the other both require the same time T. However, m and n are often quite large, and so this periodicity is on a time scale much longer than that of the natural oscillations. The behavior on a shorter time scale can be quite complex and apparently erratic as a result of the strong interaction between the oscillators. The synchronization property is demonstrated in Fig. 1B, which shows the two time-dependent voltages under conditions for which $m/n = 3/2$. The spacing between adjacent pulses is nonuniform. A graph of I_1 versus I_2 is given in Fig. 1C, which can be viewed as a two-dimensional cross section of the four-dimensional phase space composed of I_1, I_2, V_1, and V_2. This phase space trajectory, which was obtained from a time exposure of an oscilloscope trace, is clearly closed, and so the system is periodic. A more striking example is shown in Fig. 1D, where $m/n = 14/11$. This trajectory is quite complicated, but clearly closed, again indicating a strictly periodic state (*9*).

A summary of the various states which can be observed as the applied voltage is varied is shown in Fig. 1E. The ordinate is m/n, or equivalently the ratio $\bar{\nu}_1/\bar{\nu}_2$ of the mean frequencies of the two oscillators. The observed step pattern is indicative of the strong tendency toward synchronization and periodicity of this system. The solid line is the ratio of the free-running frequencies of the two oscillators, obtained by disconnecting each one in turn. When coupled, the oscillators settle into a periodic state which is relatively close to this line. The transitions between different periodic regimes often exhibit hysteresis.

We also obtained amplitude spectra for the diode voltages, using a hard-wired, real-time spectrum analyzer, as shown in Fig. 2A for the 14/11 state. (The ordinate would be squared to obtain the somewhat more conventional power spectrum.) This spectrum is composed entirely of sharp peaks. The apparent width is exaggerated by the logarithmic vertical scale but is purely instrumental. The base line is an instrumental noise level. All of the peaks are at multiples of the basic frequency $T^{-1} = 1.77$ kHz. However, most of the power is in the peak located at $\bar{\nu}_2 = 11\,T^{-1} = 19.5$ kHz. The spectrum of the other voltage is similar, except that the largest peak is at $\bar{\nu}_1 = 14\,T^{-1} = 24.8$ kHz.

If the coupling strength is reduced by about a factor of 10, the same qualitative behavior persists (*10*), although the amount of phase modulation of one oscillator by the other is reduced, and hence the integers m and n often have to be larger. It appears that synchronization and periodicity require only a very small amount of coupling. We also find that adding a third oscillator does not produce nonperiodic states, only more complex periodic ones. However, as the number of peaks in the spectrum increases, it becomes increasingly difficult to distinguish experimentally between a complex periodic state and a nonperiodic state (*11*).

We have reproduced these phenomena by a simple numerical model in which the diode voltages are assumed to be constant except when the current passes one of its threshold values. In this case, the circuit is a linear system in the intervals between voltage jumps, and exact solutions $I_1(t)$ and $I_2(t)$ can be obtained as a sum of two exponentials and a constant. One determines the times of voltage discontinuities by repetitively determining the root of an algebraic equation, and the coefficients in the solution are recomputed for each successive time interval. This method, which avoids numerical integration, permits exceed-

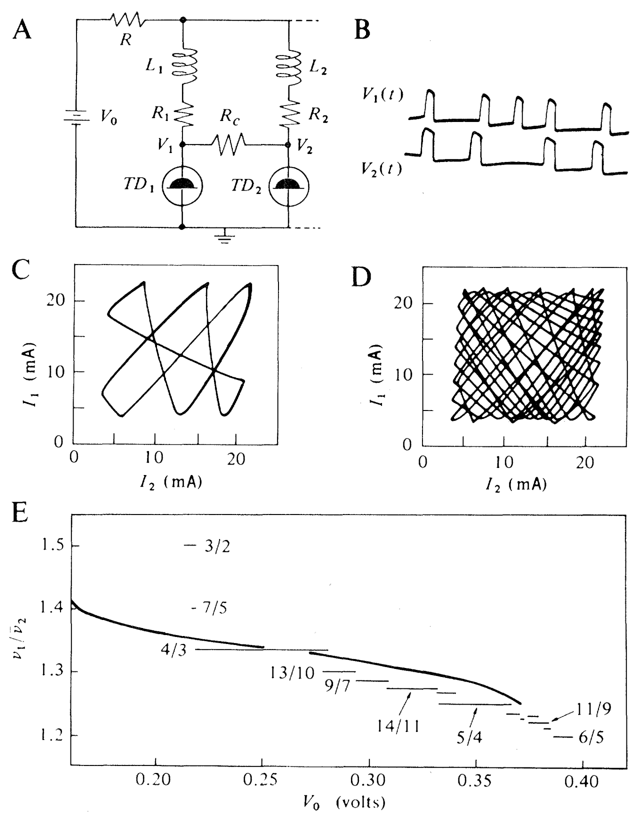

Fig. 1. (A) General circuit used in the experiments. Any number of tunnel diodes (*TD*) may be included. For the remainder of this figure, R_c is absent, $R = 3$ ohms, $L_1 = 231$ μH, $L_2 = 336$ μH, $R_1 = 1.3$ ohms, and $R_2 = 1.4$ ohms. However, none of these values are critical. (B) Diode voltages $V_1(t)$ and $V_2(t)$ showing synchronization in a periodic state with $m/n = 3/2$. (C) Phase space trajectory corresponding to (B) projected onto the plane containing the two diode currents I_1 (ordinate) and I_2 (abscissa). The upper and lower bounds for these variables are 22 mA and 3 mA. (D) Phase space trajectory for a more complicated, but still periodic, 14/11 state. (E) Ratio of the mean frequencies of the two oscillators, or equivalently the ratio m/n, as a function of V_0.

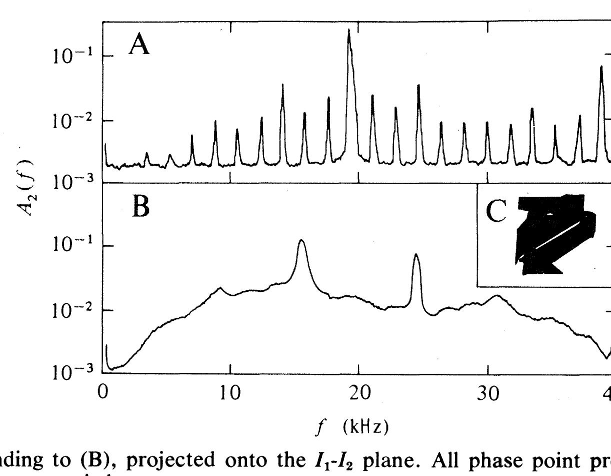

Fig. 2. (A) Amplitude spectrum of the diode voltage $V_2(t)$ corresponding to the complex periodic state of Fig. 1D. The width of the peaks on this logarithmic scale is purely instrumental. (B) Amplitude spectrum of $V_2(t)$ at $V_0 = 0.2006$ V for a circuit having $R = 0$, $R_c = 100$ ohms, $L_1 = 231$ μH, and $L_2 = 417$ μH. None of these values are critical. The peaks actually have a width greater than 100 Hz, and the time evolution is nonperiodic. (C) Phase space trajectories corresponding to (B), projected onto the I_1-I_2 plane. All phase point projections in the solid region are occupied.

ingly accurate numerical solutions to be obtained over hundreds of cycles or more. If parameters similar to those of the actual circuit are used, these computations show the phenomena of synchronization and periodicity described above.

States with intrinsic noise can be produced by a second coupling scheme which incorporates a finite value of R_c. In this case, a change in one of the diode voltages will immediately change the other diode current, rather than simply affecting its rate of change, as in the circuit with coupling provided by the resistor R. We now find that the trajectories are no longer periodic for certain broad ranges of applied voltage. The spectra contain a great deal of broadband noise (Fig. 2B). Although several peaks are still visible, high-resolution spectra show even the sharpest one to have a full width at half maximum of about 100 Hz. (In the periodic states the spectral lines have widths of a few hertz at most, and perhaps much less.) The corresponding phase space projection (Fig. 2C) uniformly fills an irregularly shaped region of the I_1–I_2 plane. This behavior is clearly nonperiodic, and is qualitatively different from the states described above. Although it is not difficult to find physical parameters that yield this type of chaos, only periodic states are observed if the system is scaled down to much lower frequencies (by increasing the inductances). In this physically realizable dissipative dynamical system, we have shown experimentally that the nature of the coupling is much more important than the number of degrees of freedom in generating chaos.

J. P. GOLLUB
T. O. BRUNNER
B. G. DANLY

Physics Department, Haverford College, Haverford, Pennsylvania 19041

References and Notes

1. For a review of the statistical behavior of simple conservative Hamiltonian systems, see J. Ford, in *Fundamental Problems in Statistical Mechanics*, E. G. D. Cohen, Ed. (North-Holland, Amsterdam, 1975), vol. 3, p. 215.
2. E. N. Lorenz, *J. Atmos. Sci.* **20**, 130 (1963).
3. R. M. May, *Science* **186**, 645 (1974).
4. M. C. Mackey and L. Glass, *ibid.* **197**, 287 (1977).
5. C. F. F. Carney and A. Bers, *Phys. Rev. Lett.* **39**, 550 (1977).
6. A. E. Cook and P. H. Roberts, *Proc. Cambridge Philos. Soc.* **68**, 547 (1970).
7. J. B. McLaughlin and P. C. Martin, *Phys. Rev. Lett.* **33**, 1189 (1974); *Phys Rev. Sect. A* **12**, 186 (1975); D. Ruelle and H. Takens, *Commun. Math. Phys.* **20**, 167 (1971); E. N. Lorenz, *J. Atmos. Sci.* **20**, 448 (1963); J. P. Gollub and H. L. Swinney, *Phys. Rev. Lett.* **35**, 927 (1975); H. E. Huppert, *Nature (London)* **263**, 20 (1976).
8. The behavior of a single nonlinear oscillator is discussed extensively in C. Hayashi, *Nonlinear Oscillations in Physical Systems* (McGraw-Hill, New York, 1964).
9. The phase locking of a single nonlinear oscillator to an external periodic signal, a related phenomenon, was first discussed by B. van der Pol [*Philos. Mag.* **3**, 65 (1927); *Proc. Inst. Radio Eng.* **22**, 1051 (1934)]. In contrast to the behavior reported here, lasers are nonlinear oscillators capable of simultaneous oscillation at several incommensurate frequencies [see W. E. Lamb, Jr., *Phys. Rev.* **134**, A1429 (1964)].
10. Even the lead resistances provide sufficient coupling to cause synchronization and periodicity of this system.
11. This situation also occurs in a well-known model of the onset of turbulence suggested by L. D. Landau, *C.R. (Dokl.) Acad. Sci. URSS* **44**, 311 (1944).
12. We are indebted to R. Landauer for an unpublished manuscript suggesting these experiments and W. C. Davidon for helpful discussions. This work was supported by NSF grant ENG76-82511 and by the Research Corporation.

6 October 1977; revised 16 December 1977

Muscular Dystrophy: Inhibition of Degeneration in vivo with Protease Inhibitors

Abstract. *The protease inhibitors leupeptin and pepstatin were used in vivo in genetically dystrophic chickens to determine their effects on the histological and biochemical changes observed in this disease. These compounds appear to delay the degeneration of muscle tissue which is characteristic of this disorder and thus may have potential therapeutic value in the treatment of muscular dystrophy.*

A striking feature of muscular dystrophy is the extensive loss of sarcoplasmic and contractile proteins and their replacement by fat and connective tissue. The mechanism involved in this degradation is unknown but a persistent observation in neuromuscular degenerative disorders has been a marked elevation in the activity of acidic and neutral proteases and other lysosomal hydrolases (*1*).

We recently reported that the use of the protease inhibitors pepstatin and leupeptin (*2, 3*) could delay the degeneration of both normal and dystrophic muscle cell cultures. We thought that because of their low toxicity and nonimmunogenic nature these inhibitors might have potential therapeutic value for the treatment of muscular dystrophy and other degenerative muscle diseases. Therefore, we studied the effects of protease inhibitors in vivo in genetically dystrophic chickens.

The chickens, both normal and dystrophic, were hatched in our facilities from eggs supplied by L. Pierro, University of Connecticut, Storrs. The chicks

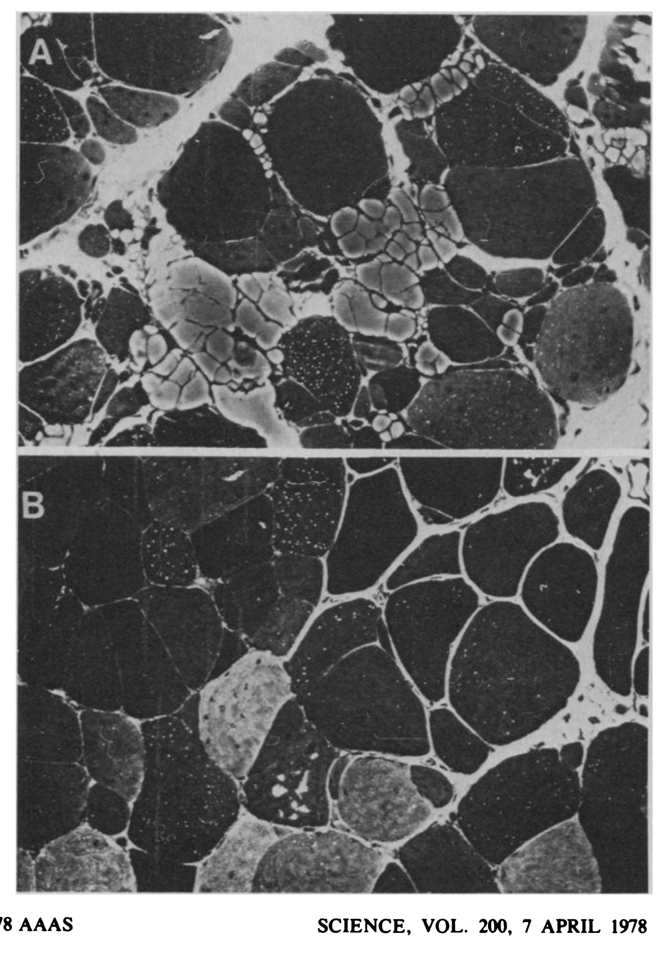

Fig. 1. Light micrographs of transverse sections of dystrophic pectoralis major muscle from an untreated 4-month-old chick (A) and from a chick injected with pepstatin and leupeptin for 4 months (B) (× 280).