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C. Kittel

Citation: Am. J. Phys. **37**, 917 (1969); doi: 10.1119/1.1975930
View online: http://dx.doi.org/10.1119/1.1975930
View Table of Contents: http://ajp.aapt.org/resource/1/AJPIAS/v37/i9
Published by the American Association of Physics Teachers

scope was triggered by a transient produced by the xenon pump lamp in the laser head. The sweep was delayed 250 μsec from this trigger signal.

Figure 5 represents a typical group of pulses

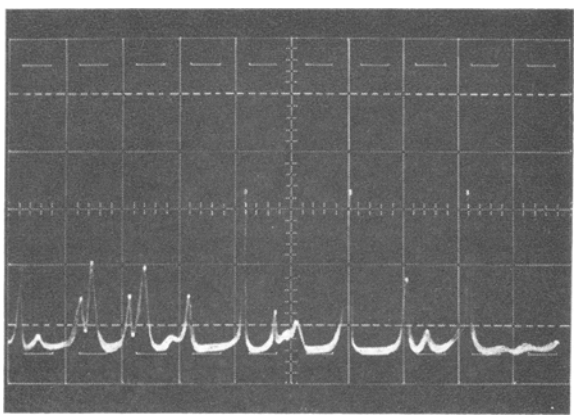

FIG. 5. A portion of a ruby-laser pulse: 2 μsec/cm sweep speed.

viewed with a somewhat faster sweep speed. The oscilloscope settings for this photograph were as follows: sweep speed, 2 μsec/cm; amplitude, 0.5 V/cm. The response of the detection system is more than adequate for use with this ruby laser. The Fairchild 100 MHz oscilloscope which we used is, of course, much more sophisticated than it need be for the student laboratory. Furthermore, one does not need a variable, delayed sweep, since it is possible to trigger off one of the early spikes in the pulse rather than off the pump-light transient. However, in choosing an inexpensive oscilloscope for use with fast pulses, it is often convenient if the vertical amplifier has a built in signal delay such as is available with the Heath 10W-14. This permits one to view the leading edge of a pulse and is a feature often missing in inexpensive oscilloscopes. A standard bezzel is also necessary if one wishes to use a scope camera without having to build up a special adapter.

CONCLUSION

In conclusion, the new photodiodes from Hewlett–Packard, together with the simple transistor amplifier designed by their technical staff, constitute a versatile, inexpensive, optical detector for student laboratories. The detector response is better than 36 nsec and is, therefore, more than adequate for use in pulsed-ruby laser studies.

AMERICAN JOURNAL OF PHYSICS VOLUME 37, NUMBER 9 SEPTEMBER 1969

Phase Transition of a Molecular Zipper*

C. KITTEL

Department of Physics, University of California, Berkeley, California 94720

(Received 7 April 1969)

Two systems of biomolecules in solution are known to be represented by simple models which can be solved to give phase transitions in one dimension. The systems are double-stranded DNA and the helical polypeptides. We treat the very simple problem of the single-ended zipper. There is an interesting simialrity with the work of Nagle on the one-dimensional analog of the Slater model of KDP.

The zipper model is an unusually simple and interesting member of the class of one-dimensional systems which exhibit a phase transition. The double-ended zipper, in which unwinding is permitted from both ends, was discussed first by Gibbs and DiMarzio[1] in connection with two problems in statistical mechanics: the uncoiling of the helical conformation of a polypeptide chain, and the separation of the two strands of the double-stranded helix of desoxyribonucleic acid

* Supported by the Office of Naval Research Contract 3656(30).

[1] J. H. Gibbs and E. A. Dimarzio, J. Chem. Phys. **30**, 271 (1959); see also D. M. Crothers, N. R. Kallenbach, and B. H. Zimm, J. Mol. Biol. **11**, 802 (1965),

(DNA). In long lengths of natural DNA and also in related synthetic polymers the two strands may separate in interior regions as well as at their ends, so that the zipper model is oversimplified. Experiments on the transition have been carried out on DNA of molecular weight as high as 10^8. There is a considerable literature concerned with the transition of DNA in solution as the temperature is varied or as the pH is varied; we are content here to list selected references[2] and to exhibit one experimental curve (Fig. 1).

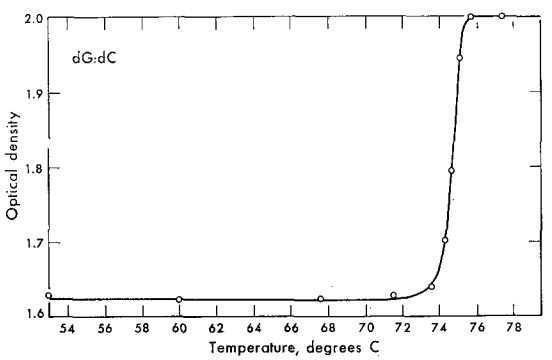

FIG. 1. Unwinding transition from double-stranded to single-stranded synthetic DNA-like polymer of dG:dC, from an experimental curve by Baldwin and coworkers. At low temperatures the system is double-stranded. The optical absorption is used as a measure of the state of the system. For further experimental curves, see R. B. Inman and R. L. Baldwin, J. Mol. Biol. **8,** 452 (1964).

The single-ended zipper is simpler than any related problem which has been treated, and it offers a good way to introduce a biophysics example into a course on statistical physics. There may arise actual situations to which the solution applies qualitatively. We treat a molecular zipper of N parallel links that can be opened only from one end (Fig. 2). If the links 1, 2, $\cdots$, p are all open,

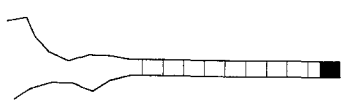

FIG. 2. Open and closed links in a single-ended zipper.

[2] S. A. Rice and A. Wada, J. Chem. Phys. **29,** 233 (1958); J. H. Gibbs and E. A. DiMarzio, Ref. 1; T. L. Hill, J. Chem. Phys. **30,** 383 (1959); B. H. Zimm **33,** 1349 (1960); D. M. Crothers and B. H. Zimm, J. Mol. Biol. **9,** 1 (1964); S. Lifson and B. H. Zimm, Biopolymers **1,** 15 (1963); N. S. Goel, Tech. Rept. No. 462, University of Maryland, 1965; S. Lifson, Biopolymers **1,** 25 (1963); S. Lifson and G. Allegra, *ibid.* **2,** 65 (1963); S. Strässler, J. Chem. Phys. **46,** 1037 (1967).

the energy required to open the $p+1$st link is ϵ. However, if all the preceding links are not open, the energy required to open the $p+1$st link is infinite. We specify further that the last link, $p=N$, cannot be opened; this minor feature serves only to distinguish one end from the other, and we shall say that the zipper is open when $N-1$ links are open. We suppose that there are G orientations which each open link can assume: that is, the open state of a link is G-fold degenerate, corresponding to the rotational freedom of a link. There will be no phase transition if $G=1$, as we shall see below. In the problem of DNA the empirical value of G may be of the order of 10^4. More generally, it may be shown that $G \equiv \exp[\Delta f/\tau]$, where Δf is the difference of free energy of a single link in the closed and open configurations.

PARTITION FUNCTION

The energy required to open the first p links is $p\epsilon$. If p links are open, the degeneracy is G^p, and the contribution of this configuration to the partition function is $G^p \exp(-p\epsilon/\tau)$. The partition function is

$$Z = \sum_{p=0}^{N-1} G^p \exp(-p\epsilon/\tau) ; \tau \equiv k_B T, \qquad (1)$$

which may be summed to give

$$Z = (1-x^N)/(1-x); \qquad x \equiv G \exp(-\epsilon/\tau). \qquad (2)$$

It is dangerous to write $Z=(1-x)^{-1}$ as the partition function for $N=\infty$; the correct procedure is to evaluate thermodynamic quantities for finite N and then to examine the limit.

NUMBER OF OPEN LINKS

The thermodynamic average number of open links is

$$\langle s \rangle = \sum p x^p / \sum x^p = x(d/dx) \log Z$$
$$= [Nx^N/(x^N-1)] - [x/(x-1)]. \qquad (3)$$

This function is plotted in Figs. 3 and 4 for $N=1024$. We examine the behavior of $\langle s \rangle$ in the vicinity of the point $x_c=1$ for which the denominators in Eq. (3) are zero. With $x \equiv 1+\eta$, we have

$$\log Z \cong \log N + \tfrac{1}{2}N\eta + \tfrac{1}{24}N^2\eta^2 - \tfrac{1}{2880}N^4\eta^4 + \cdots, \qquad (4)$$

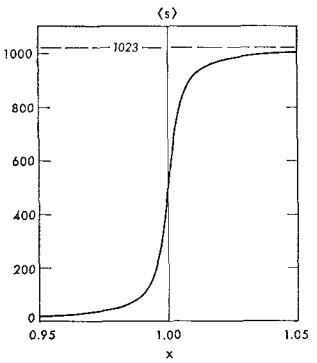

FIG. 3. Thermodynamic average number of open links in a single-ended zipper of $N=1024$ links. Here $x \equiv G\exp(-\epsilon/k_BT)$, with G the degeneracy of an open link and ϵ the energy required to open a link. For small changes in x around $x_c=1$ we have $x-x_c \propto T-T_c$.

by series expansion. Then

$$\langle s\rangle = G(d\eta/dG)\,(d/d\eta)\,\log Z$$

$$\cong \tfrac{1}{2}N(1+\tfrac{1}{6}N\eta-\tfrac{1}{360}N^3\eta^3+\cdots), \qquad (5)$$

for $N\gg 1$ and $\eta \ll 1$. We see that $\langle s\rangle = \frac{1}{2}N$ at the transition point defined as $x_c=1$, where $\eta=0$. The fractional slope

$$(1/N)\,(d\langle s\rangle/d\eta)\cong \tfrac{1}{12}N-\tfrac{1}{240}N^3\eta^2+\cdots, \qquad (6)$$

is a maximum at $\eta=0$, and the slope at the transition point becomes infinite as $N\to\infty$.

TRANSITION TEMPERATURE

If $G=1$, there is no solution at a finite temperature τ to the transition point equation

$$G\exp(-\epsilon/\tau_c)=1; \qquad \tau_c=\epsilon/\log G. \qquad (7)$$

There is a finite transition temperature if $G>1$. One might perhaps argue that the model is now not strictly one-dimensional, for the degeneracy G arises from the rotational freedom of an open link.

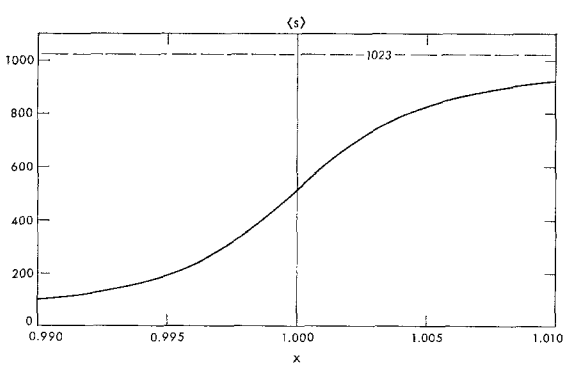

FIG. 4. Transition region of Fig. 3 on an expanded scale.

In this respect the model is not unlike the Nagle[3] model of the ferroelectric KH_2PO_4, where the degeneracy of the allowed proton configuration about a PO_4 group is essential to the transition. The existence of forbidden (infinite energy) configurations is a necessary, but not sufficient, condition for a phase transition in a one-dimensional system with a finite range of force. A further requirement may be that the degeneracy of the excited state of a structural unit must be higher than the degeneracy of the ground state.[4]

For small values of η (such as those involved in Figs. 3 and 4) we have an approximate proportionality of η to $\tau-\tau_c$. From expression (7) we find

$$\eta\cong \frac{\epsilon}{\tau_c}\cdot\frac{\tau-\tau_c}{\tau_c} = (\log G)\cdot\frac{\tau-\tau_c}{\tau_c}, \qquad (8)$$

for $\eta\ll 1$.

For $x\gg 1$ we find from Eq. (3) the limiting form

$$\langle s\rangle\cong(N-1)-1/(x-1)=(N-1)-1/\eta, \qquad (9)$$

so that $\langle s\rangle$ approaches hyperbolically its limiting value $N-1$, and the zipper is unwound. For $x\ll 1$ we have

$$\langle s\rangle\cong x/(1-x), \qquad (10)$$

independent of N.

CHAINS WITH ALL LINKS OPEN

It may come as a surprise that the number of open chains at the transition is very small. An open chain has $N-1$ open links, and the probability P of this event is

$$P=x^{N-1}/Z=x^{N-1}[(x-1)/(x^N-1)]. \qquad (11)$$

Very close to the transition $N\eta\ll 1$; here

$$P\cong N^{-1}+\eta, \qquad (12)$$

[3] J. F. Nagle, Amer. J. Phys. **36,** 1114 (1968), has shown that the one-dimensional analog of the Slater model of KDP has a first-order transition. The partition function for this problem is essentially identical with that of a zipper which has two configurations, all links open or all links closed, as discussed by T. M. Birshtein and O. B. Ptitsyn, *Conformations of Monomolecules* (Wiley-Interscience Inc., 1966), Chap. 9.

[4] In the mean-field approximation no transition can occur if the degeneracy of the ground state is higher than that of the excited state: S. Strässler and C. Kittel, Phys. Rev. **139A,** 758 (1965).

and at the transition

$$P(x_c)=1/N. \tag{13}$$

Only one chain in N is open at the transition. The development of open chains above the transition is only a weak function of the temperature: For $x^N \gg 1$,

$$P \cong 1-x^{-1}. \tag{14}$$

Function (11) is plotted in Fig. 5.

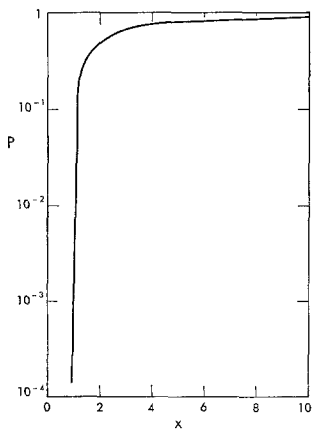

FIG. 5. Probability P that 1023 links are open, for a zipper of $N=1024$ links. We assume the last link cannot be opened.

ENTROPY

The entropy of the system is given by

$$\sigma=\tau(\partial/\partial\tau)\ \log Z+\log Z$$
$$=[x\log(G/x)](d/dx)\ \log Z+\log Z. \tag{15}$$

Here σ is the conventional entropy divided by k_B. From expression (2) we find

$$\sigma=\langle s\rangle\log(G/x)+\log(x^N-1)-\log(x-1), \tag{16}$$

but in the interesting region near the transition this reduces to

$$\sigma\cong\langle s\rangle\log G, \tag{17}$$

provided $N\eta\ll 1$. In the region of the transition, the entropy is proportional to the average number of open links as given by expression (5) and as plotted in Figs. 3 and 4.

The heat capacity is $C=k_B\tau d\sigma/d\tau$, and in the region of the transition

$$C\cong k_B(\log G)^2 d\langle s\rangle/d\eta$$
$$\cong Nk_B(\log G)^2[\tfrac{1}{12}N-\tfrac{1}{240}N^3\eta^2+\cdots], \tag{18}$$

provided $N\eta\ll 1$. The heat capacity per link becomes infinite as $N\to\infty$. The transition is essentially first order.

UNWINDING FROM BOTH ENDS

When the zipper is allowed to unwind from both ends, there are $p+1$ ways in which a total of p links may be opened, so that the partition function for a double-ended zipper of N links is

$$Z=\sum_{p=0}^{N-1}(p+1)G^p\exp(-p\epsilon/\tau), \tag{19}$$

and to this should be added a term for the state of N open links. This terminal term for a simple zipper is $G^N\exp(-N\epsilon/\tau)$; for a single polypeptide chain the term is $G^{N+2}\exp(-N\epsilon/\tau)$, as discussed by Gibbs and DiMarzio.[1] The terminal contribution may be omitted if the chain is long, and we may sum Eq. (19) to obtain

$$Z=[1-(N+1)x^N+Nx^{N+1}]/(1-x)^2. \tag{20}$$

With $x=1+\eta$, we have

$$\log Z\cong\log\tfrac{1}{2}N^2+\tfrac{2}{3}N\eta+\tfrac{1}{36}N^2\eta^2+\cdots, \tag{21}$$

for the transition region $N\eta\ll 1$. The number of open links near the transition of the double-ended zipper is

$$\langle s\rangle=\tfrac{2}{3}N(1+\tfrac{1}{12}N\eta+\cdots), \tag{22}$$

which may be contrasted with the result in expression (5) for the single-ended zipper. The nature of the transition does not appear to be altered.

ACKNOWLEDGMENT

I am grateful to Dr. H. E. Stanley for checking parts of the calculations.