AUGUST 1, 1930 *PHYSICAL REVIEW* *VOLUME 36*

COUPLED VIBRATIONS WITH APPLICATIONS TO THE SPECIFIC HEAT AND INFRARED SPECTRA OF CRYSTALS

By Arthur B. Lewis
The Johns Hopkins University

(Received June 23, 1930)

Abstract

The free periods of certain coupled systems of linear oscillators are considered in this paper. The complete system discussed consists of p identical, coupled, groups; each group containing n identical linear oscillators. The equations of motion of such a system lead to a determinantal equation of the pn^{th} order, of which the well-known determinantal equations of the uniformly loaded string and the finite wave filter are special cases. The solution of this general determinantal equation has been reduced to the solution of certain trigonometric equations. A solution for the free periods of the system is obtained for the case in which the coupling between the groups is small compared to the internal forces of the groups. In case only one or two groups are present the resulting equations can be solved readily to any desired degree of approximation for any values of the forces whatever. Certain special cases are noted in which, for special values of the forces, exact solutions become possible.

Sample calculations have been carried out which illustrate the behavior of the pn free periods of a system of pn particles when various forces act between the particles of the system, and when the pn particles are rearranged in various ways. With the aid of the equations obtained above the specific heats of four of the normal alcohols have been computed at low temperatures and compared with the experimentally determined values. A reasonable agreement is obtained between the observed and computed values, but with the data at hand the agreement cannot be said to be conclusive.

1. Introduction

RECENT investigators in the infrared spectra of organic compounds[1,2] have attained considerable success in organizing their data by assigning certain prominent bands which are common to all organic compounds to certain modes of vibration between the component parts of the molecules under investigation. It is generally agreed that the strong band at about 3.5μ in the spectra of organic compounds is to be identified with the vibration of the hydrogen atom against the carbon atom. Similarly the band at about 28μ is to be identified with the vibration of carbon against carbon. This assumption of the spring-like nature of these chemical bonds is supported by several lines of evidence. The assignment of a characteristic frequency to a given bond permits the calculation of the force constant of the bond. This in turn leads to the calculation of the heat of linkage.[3] There is good agree-

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[1] J. W. Ellis, Phys. Rev. **23,** 48 (1924); **27,** 298 (1926), **28,** 25 (1926).

[2] J. W. Sappenfield, Phys. Rev. **33,** 37 (1929).

[3] Grundriss der Phys. Chem., A. Eucken, p. 459ff(1924) (References) J. W. Ellis, Phys. Rev. **33,** 27 (1929).

ment between the observed and computed values. Moreover these characteristic frequencies, when used in Einstein's formula,[4] and Debye's formula,[5] should give the specific heat curve of the compound at low temperatures. There seems to be reasonably good agreement between the computed curves and the observed values.[6]

It has therefore seemed worthwhile to consider a little more closely the free periods of vibration which one would expect from a mechanical model of one of these molecules, or from a group of molecules. To this end we shall consider the molecules under discussion as being represented by a series of massive particles attached at regular intervals to a massless elastic string. We shall first determine the free periods of a single group of massive particles, or of a single molecule, when various restrictions are placed on the ends of the molecule or group. We shall next consider the effect upon these periods of coupling two or more molecules or groups together, and shall thus determine the free periods of a system consisting of a number of identical molecules or groups coupled together. Such a system may be realized in the crystals of organic chain compounds. We shall finally be able to obtain the free periods of a single group of pn particles, and then to determine the effects produced on these frequencies by rearranging the pn component particles into various groupings (such as p groups of n particles each) keeping the total number of particles present always the same.

Mathematically we have here an extension of the problem of the vibration of a loaded string which has been treated by Lagrange,[7] Lord Rayleigh,[8] and others. The second order differential equations which arise from this problem are similar to those which arise in the solutions of the modes of vibration of other systems, particularly in the solution of wave filter problems. The analogous electrical case of the finite wave filter has been treated by Pupin,[9] Campbell,[10] Carson,[11] Wheeler and Murnaghan,[12] and others.

The method of solution consists, as usual, in setting up the differential equations of motion, which can be solved for periodic vibrations if a certain algebraic equation equals zero. This equation is known as the secular or characteristic equation. The roots of this equation give the frequencies of the free vibrations. In what follows we shall limit ourselves to motion in one dimension. In general, under these conditions, a system of N particles will possess N frequencies. If the system is free to move as a whole, or to rotate uniformly, the corresponding frequency is zero.

The system of particles which we shall discuss is obtained by arranging

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[4] A. Einstein, Ann. d. Physik **28,** 180 (1907).

[5] P. Debye, Ann. d. Physik **39,** 789 (1912).

[6] D. H. Andrews, Proc. Roy. Acad. Amsterdam **29,** 744 (1926); Chemical Reviews **5,** 533 (1928).

[7] Mecanique Analytique, Lagrange, vol. 1, pp. 382–395 (1811).

[8] Theory of Sound, Lord Rayleigh; vol. 1, p. 120 (1877).

[9] M. Pupin, Proc. A.I.E.E. **16,** 93 (1899).

[10] G. A. Campbell, Bell System Tech. J. p. 1, November 1922.

[11] Electric Circuit Theory and Operational Calculus, Carson, p. 132 ff. (1926).

[12] H. A. Wheeler and F. D. Murnaghan, Phil. Mag. **6,** 146 (1928).

pn equal particles into p groups of n particles each. We now introduce a small quantity, d, which we call the "coupling coefficient" and which measures the ratio of the force acting between the groups to the force inside of the group. An inspection of Fig. 1 will indicate that when $d=1$ the forces acting between the groups are the same as the forces acting within the groups, there is not longer any distinction between "groups," and we have the elementary case of the uniformly loaded string. The situation existing when $d=0$ must be examined with a little more care since d is defined as the ratio of two quantities. If d vanishes due to the fact that the internal forces present in each group are infinite we must say that we no longer have any vibrating group structure present. Our system will therefore vibrate as a uniformly loaded string of p particles, each of mass nm, the force constant of the string being that of the inter-group force. We have present the p frequencies characteristic of these p groups, while the other $p(n-1)$ internal frequencies have been shifted to infinity. On the other hand if d vanishes due to the fact that the force between the groups has become infinitely small we must say that we have p groups present as before, but each infinitely removed from its neighbors and therefore entirely unaffected by them. We shall therefore expect the pn free periods of such a system to be the n free periods of a single group of n particles with free ends, each free period being repeated p times. These n frequencies characteristic of a single group of n particles with free ends will consist of one frequency, $\nu=0$, which corresponds to the vibration. When d has become small, but both forces remain finite, we can predict in a general way the behavior of the free periods. The p slowest vibrations will be slight modifications of the p vibrations which would be present if each group vibrated as a rigid whole, and on the other hand can be considered as corresponding to the p vibrations of frequency 0 for the p free molecules or groups. Similarly the $p(n-1)$ faster vibrations will be slight modifications of, and will therefore group themselves about, the $(n-1)$ internal vibrations which would be present if each group were entirely separated from its neighbors. While these, however, had been p-fold in the case of the independent molecules or groups, these p coinciding frequencies will be split up now into p separate components by the effect of the coupling.

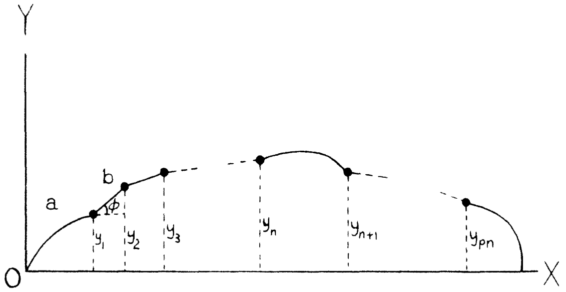

Fig. 1.

II. STATEMENT OF THE MATHEMATICAL PROBLEM

Let us consider the motion of a massless, elastic string on which are fastened a number of massive particles of common mass "m". Let these particles be arranged in identical and recurring groups of "n" particles, the common distance between particles of the same group being b. Let the distance between the n^{th} particle of any one group and the 1^{st} particle of the next group be a, there being p groups in all, see Fig. 1. Let the initial, uniform, tension in the string be T. Let us confine ourselves for the moment to small lateral displacements, all in the same plane, these displacements being so small that we may replace the sines of the angles by the angles themselves. This means that we can say, Fig. 1,

$$\sin\phi = \tan\phi = (y_r - y_{r-1})/a \text{ or } (y_r - y_{r-1})/b$$

We will so choose our axes that $y_0 = y_{pn+1} = 0$.

It is to be noted here that the introduction of the concept of an elastic spring under tension is a matter of convenience and not of necessity. In the same way we have restricted ourselves to small vertical displacements from convenience and not from necessity, We might have started equally well with a system of identical groups of particles in equilibrium under the influence of quasielastic restoring forces of any origin whatever. We have in this case to define a force constant which will be the restoring force per unit displacement acting on the r^{th} particle due to its displacement with respect to the $(r+1)^{st}$ or $(r-1)^{st}$ particle. This force constant we may call τ when the neighboring particle under consideration belongs to the same group as the r^{th} particle, and τ' when the neighboring particle under consideration does not belong to the same group as the r^{th} particle. The equations which will be obtained as Eqs. (1) will be found to follow immediately with the replacing of T/a and T/b by τ' and τ respectively. It will be noted in the following equations that the tension T always occurs in the expression T/a or T/b, which has the dimensions $F.L^{-1}$ as it should. It is apparent from what has been said that our coordinates y_r may be looked upon as generalized coordinates, the quantities which will occur in Eqs. (1) as $m\ddot{y}$ may be looked upon as generalized inertial forces, and the corresponding expressions such as $T/b(-y_{r-1}+2y_r-y_{r+1})$ may be looked upon as generalized forces of restitution. The equations which will be obtained as Eqs. (1) are then equally capable of representing motions along the axis of X, perpendicular to the axis of X, rotations about this axis, or oscillations in properly coupled electrical circuits. The quantity defined as "d", Eq. (3) will be given, in the light of the definitions of this paragraph as τ'/τ.

We can now write down the expressions for the kinetic and potential energy of the system,[13] and set up the equations of motion by Lagrange's equations,

$$T - V = L$$

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[13] Partial Differential Equations of Mathematical Physics, Webster, p. 91, (1927).

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{y}_r}\right) - \frac{\partial L}{\partial y_r} = 0.$$

More simply we may resolve the forces parallel to the direction of y and obtain, after a little rearrangement,

$$\begin{aligned}
&m\ddot{y}_1 + (T/a)y_1 + T/b(y_1 - y_2) = 0\\
&m\ddot{y}_2 + T/b(-y_1 + 2y_2 - y_3) = 0\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&m\ddot{y}_n + T/b(y_n - y_{n-1}) + T/a(y_n - y_{n+1}) = 0\\
&m\ddot{y}_{n+1} + T/a(y_{n+1} - y_n) + T/b(y_{n+1} - y_{n+2}) = 0\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned}\tag{1}$$

We now make the usual substitution

$$y_r = C_r \exp\left(-\lambda^{1/2}t\right). \tag{2}$$

Divide the equations by the common factor $\exp((-\lambda)^{1/2}t)$, and multiply by the common factor b/T. The following definitions become obvious,

$$\begin{aligned}
(-mb\lambda)/T + 2 &= A\\
(-mb\lambda)/T + 1 + b/a &= B\\
b/a &= d
\end{aligned}\tag{3}$$

Manifestly

$$1 + d - 1 = B.$$

Making the substitutions indicated in Eq. (3) and rearranging terms we obtain from Eq. (1),

$$\begin{aligned}
BC_1 - C_2 &= 0\\
-C_1 + AC_2 - C_3 &= 0\\
-C_2 + AC_3 - C_4 &= 0\\
\cdots\cdots\cdots\cdots&\cdots\\
\cdots\cdots\cdots\cdots&\cdots\\
-C_{n-2} + BC_{n-1} - dC_n &= 0\\
-dC_{n-1} + BC_n - C_{n+1} &= 0\\
\cdots\cdots\cdots\cdots&\cdots\\
\cdots\cdots\cdots\cdots&\cdots\\
-C_{pn-1} + BC_{pn} &= 0.
\end{aligned}\tag{4}$$

The condition for a solution giving values for the C's other than zero is that the determinant of the coefficients shall vanish. This gives a determinant of the pn^{th} order which we shall designate as F_p. It is to be understood by this notation that F_p represents the determinant of the pn^{th} order obtained from Eqs. (4) written for p identical groups of n particles each. We shall not be interested in this particular determinant when there are not exactly n particles in each group. The determinantal equation is

$$F_p=\left|\begin{array}{cccccccccccc}
B & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
-1 & A & -1 & 0 & 0 & 0 & 0 & 0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & -1 & A & -1 & 0 & 0 & 0 & 0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & 0 & -1 & B & -d & 0 & 0 & 0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & 0 & 0 & -d & B & -1 & 0 & 0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & 0 & 0 & 0 & -1 & A & -1 & 0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & A & -1 & 0\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & B & -d\cdot\cdot & & \cdot\cdot 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -d & B\cdot\cdot & & \cdot\cdot 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & -1 & A & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 & -1 & A & -1 & 0 & 0 & 0 & 0 \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 & 0 & -1 & B & -d & 0 & 0 & 0 \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 & 0 & 0 & -d & B & -1 & 0 & 0 \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 & 0 & 0 & 0 & -1 & A & -1 & 0 \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 & 0 & 0 & 0 & 0 & -1 & A & -1 \\
0 & 0\cdot\cdot & & \cdot\cdot 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & B
\end{array}\right| \begin{array}{l} =0 \quad (5) \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ pn^{th} \\ \text{order} \\ \\ \\ \\ \end{array}$$

For convenience the groups have been represented as having a limited number of terms, $n=4$.

This determinant is a function of the unknown $\lambda(=2\pi\nu^2$ where ν is the frequency) which is the variable entering through the quantities A and B. The solution of the problem will consist in finding those values of λ which will reduce the determinant to zero. A direct expansion of Eq. (5) will lead to an algebraic equation of the pn^{th} degree in λ. If it were possible to solve this algebraic equation, the resulting pn roots of λ would lead to the pn desired free periods of the system. This is the number of free periods which we expect from the number of degrees of freedom possessed by the system. Such a direct method of solution is not feasible in general. We must therefore look for transformations which will reduce Eq. (5) to a more tractable form. The general method of attack has been pointed out by Wheeler and Murnaghan.[12] The method consists essentially in reducing the expansion of Eq. (5) to a trigonometric equation in which the unknown, θ, is defined as a function of λ. The resulting trigonometric equation is well adapted to the processes of approximation.

An inspection of the determinant F_p will disclose that it is made up of certain simpler and recurring groups. As will be seen later the expansion of the complete determinant is obtained in terms of these sub-groups. We shall therefore define the following determinants:

$$D_n(d,\,d) = \begin{vmatrix} B & -1 & 0 & 0 & 0\cdots & & & & & \cdots 0 \\ -1 & A & -1 & 0 & 0\cdots & & & & & \cdots 0 \\ 0 & -1 & A & -1 & 0\cdots & & & & & \cdots 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0\cdots & & & & \cdots 0 & -1 & A & -1 & 0 \\ 0 & 0\cdots & & & & \cdots 0 & 0 & -1 & A & -1 \\ 0 & 0\cdots & & & & \cdots 0 & 0 & 0 & -1 & B \end{vmatrix} \quad n^{\text{th}} \text{ order} \qquad (6)$$

$$D_n(1,\,d) = \begin{vmatrix} A & -1 & 0 & 0\cdots & & & & & \cdots 0 \\ -1 & A & -1 & 0\cdots & & & & & \cdots 0 \\ 0 & -1 & A & -1\cdots & & & & & \cdots 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0\cdots & & & \cdots 0 & -1 & A & -1 & 0 \\ 0 & 0\cdots & & & \cdots 0 & 0 & -1 & A & -1 \\ 0 & 0\cdots & & & \cdots 0 & 0 & 0 & -1 & B \end{vmatrix} \quad n^{\text{th}} \text{ order.} \qquad (7)$$

$$D_n(1,\,1) = \begin{vmatrix} A & -1 & 0 & 0\cdots & & & & \cdots 0 \\ -1 & A & -1 & 0\cdots & & & & \cdots 0 \\ 0 & -1 & A & -1\cdots & & & & \cdots 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0\cdots & & & \cdots 0 & -1 & A & -1 \\ 0 & 0\cdots & & & \cdots 0 & 0 & -1 & A \end{vmatrix} \quad n^{\text{th}} \text{ order} \qquad (8)$$

The determinant $D_n(1,1)$ is the determinant of the uniformly loaded string,[13] and of the elementary wave filter.[12] The present notation has been adopted since the determinant $D_{pn}(1,1)$, see Eq. (8), can be obtained from the general determinant F_p, Eq. (5), by putting the quantity d everywhere equal to unity. The d's then disappear from the determinant itself, and the quantity B becomes equal to the quantity A, see Eq. (3). Similarly the determinant $D_n(1,d)$ is obtained from the determinant $D_n(1,1)$ by replacing one of the A's which constitute the terminal elements of the principal diagonal by the quantity B which is $A+d-1$. In the same way the determinant $D_n(d,d)$ is obtained from the elemental determinant $D_n(1,1)$ by replacing both of the A's which constitute the terminal elements of the principal diagonal by the quantity B.

Let us now make the following definitions:*

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* The author is indebted to Prof. F. D. Murnaghan for these substitutions.

$$H_p = F_p\mu^{-p} \tag{9}$$

$$\mu = + d(D_{n-1}^2(1, d) - D_n(d, d)D_{n-2}(1, 1))^{1/2} \tag{10}$$

$$\xi = \frac{D_n(d, d) - d^2D_{n-2}(1, 1)}{\mu} \cdot \tag{11}$$

It can then be readily shown that the expansion of Eq. (5) is equivalent to

$$H_p = \xi H_{p-1} - H_{p-2}. \tag{12}$$

The condition that $F_1 = D_n(d,d)$ leads to the following definitions

$$H_0 = 1 \tag{13}$$

$$H_1 = \frac{D_n(d, d)}{\mu} \cdot \tag{14}$$

We see from an inspection of Eq. (12) and Eq. (11) that the general solution for H_p will depend upon the values assumed by the determinants which we have defined in Eqs. (6), (7) and (8). These determinants are special cases of the determinant F_p as should be evident from Eq. (5). Since a knowledge of these special cases is necessary for a complete solution, we shall digress here to consider the form assumed by F_p when we have only one group present, $p = 1$.

III. Solution of Certain Limiting Cases

(A) The uniformly loaded string (Lagrange's problem).

The solution for the free periods of the uniformly loaded string, which is given by

$$D_n(1, 1) = 0$$

where

$$p = 1$$
$$d = 1 \text{ in } Eq. (5)$$

is so well known [12,13] that we shall merely state the result here, since it will be used constantly in what follows. The determinant may be expanded yielding

$$D_n(1, 1) = AD_{n-1}(1, 1) - D_{n-2}(1, 1).$$

This gives

$$D_n(1, 1) = \frac{\sin (n + 1)\theta}{\sin \theta} \tag{15}$$

if we make the substitution

$$A = (- mb\lambda)/T + 2 = 2 \cos \theta \tag{16}$$

The solution

$$D_n(1, 1) = 0$$

is given by

$$\theta = K\pi/(n + 1), \quad K = 1, 2, \cdots, n \tag{17}$$

The values of θ given by Eq. (17) together with Eq. (16) connecting $A(\lambda)$ and θ give us the free periods of the system. There are n possible frequencies, as is necessary for n particles.

(B) The single group of n particles with $d \neq 1$ at its terminal elements.

This case may be represented physically by a molecule, as of an organic chain compound, which is restrained at its ends by quasielastic restoring forces which differ from the restoring forces acting within the molecule itself.

Let us consider the case

$$F_1 = 0.$$

The solution in this case is exactly analogous to that of the finite wave filter,[12] and will be obtained in the same way. Let us generalize and assume that the coupling coefficient d is not the same at the two ends. The determinantal equation then becomes

$$D_n(d, d') = \begin{vmatrix} B & -1 & 0 & 0 \cdots & & & \cdots 0 \\ -1 & A & -1 & 0 \cdots & & & \cdots 0 \\ 0 & -1 & A & -1 \cdots & & & \cdots 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 \cdots & & \cdots 0 & -1 & A & -1 \\ 0 & 0 \cdots & & \cdots 0 & 0 & -1 & B' \end{vmatrix} \quad n^{\text{th}} \text{ order}. \tag{18}$$

where

$$B = A + d - 1$$
$$B' = A + d' - 1$$

and all the other quantities have the same meanings as before. Direct expansion shows that

$$D_n(d, d') = D_n(1, 1) + (d + d' - 2)D_{n-1}(1, 1) + (d - 1)(d' - 1)D_{n-2}(1, 1).$$

With the aid of Eq. (15) this becomes, when $D_n(d,d') = 0$

$$D_n(d, d') = \frac{\sin(n + 1)\theta + (d + d' - 2)\sin n\theta + (d - 1)(d' - 1)\sin(n - 1)\theta}{\sin\theta} = 0 \tag{19}$$

It is apparent that Eq. (19) may be adjusted to any given values of the coupling coefficients d and d'. That is, we may now write the explicit expressions in terms of θ for $D_n(d,d)$, $D_n(1,d)$, $D_n(1,0)$, and $D_n(0,0)$ from Eq. (19). The solutions of the resulting trigonometric equations can be carried to as high a degree of approximation as is necessary. Two cases, in which an exact solution becomes possible, are of interest.

The solution for a uniformly loaded string free at one end, $D_n(1,0)$, a case which was discussed but not carried to completion by Lagrange,[7] is obtained by putting $d=1$ and $d'=0$ in Eq. (19). The equation for θ then readily reduces to

$$\frac{\cos (n+\frac{1}{2})\theta}{\cos n\theta \sin \theta/2} = 0$$

Whence

$$\theta = \frac{2k+1}{2n+1}\pi, \quad k = 0, 1, 2, \cdots, n. \tag{20}$$

The solution corresponding to $k=0$ corresponds to a rotation and expansion of the entire system about its point of support, all the particles lying on a straight line. Besides, there are $(n-1)$ oscillatory motions.

The solution for a uniformly loaded string free at both ends, $D_n(0,0)$ is obtained by putting both d and d' equal to zero in Eq. (19). The trigonometric equation then becomes

$$\tan n\theta = 0$$

Whence

$$\theta = \frac{k}{n}\pi, \quad k = 0, 1, 2, \cdots, (n-1). \tag{21}$$

The solution corresponding to $k=0$, which gives $\theta=0$ and consequently $\nu=0$, corresponds to a motion of the entire system as a rigid whole. If $k=n$, which gives $\theta=\pi$, we do not have a solution since in this case both numerator and denominator of Eq. (19) vanish and their ratio is not zero.

IV. SOLUTION OF THE GENERAL DETERMINANTAL EQUATION FOR p GROUPS, $H_p=0$

(A) Formal solution in terms of θ and Γ.

We can now proceed with the formal solution of the general determinant H_p.

$$H_p = \xi H_{p-1} - H_{p-2} \tag{12}$$

Eq. (12) is in the standard form[12] and if we make the substitution

$$\xi = 2 \cos \Gamma \tag{22}$$

the equation can be thrown into the form

$$H_p = \frac{\sin (p+1)\Gamma + d \sin (n-1)\theta/\sin\theta \times \sin p\Gamma}{\sin \Gamma} = 0. \tag{23}$$

The solution of our problem therefore consists in the solution of Eq. (23) together with our two equations of definition, Eqs. (16) and (22), which may be put in the form

$$\xi = \frac{2(1 - \cos\theta)(d - 1)\sin n\theta + 2d\sin\theta\cos n\theta}{d\sin\theta} = 2\cos\Gamma \tag{24}$$

$$A = (-mb\lambda)/T + 2 = 2\cos\theta \tag{16}$$

(B) Approximate solution of $H_p = 0$.

An exact solution of these equations is not, in general, possible. An approximate solution can be obtained, however, when the coupling coefficient d, is small. We have already found, Eq. (21), that when $d=0$ the values of θ are given by $(k/n)\pi$. Moreover, when $d=1$ the values of θ are given by $k\pi/(n+1)$, Eq. (17). We can therefore say, when d is small,

$$\theta_k = \frac{k\pi}{n} + \Delta\theta_k, \quad k = 0, 1, 2, \cdots, (n-1) \tag{25}$$

where $\Delta\theta_k$ is a small quantity of order d or less. We shall now inquire as to the values assumed by the expression occurring in Eq. (23), $d\sin(n-1)\theta/\sin\theta$, when θ has the value given by Eq. (25). Direct substitution shows that

$$\frac{d\sin(n-1)\theta}{\sin\theta} \cong d(n-1).$$

If we will restrict ourselves to cases in which $d(n-1)$ is small in comparison with unity Eq. (23) becomes $\sin(p+1)\Gamma +$ (a small quantity of order dn) $\sin p\Gamma = 0$. An approximate solution for Γ will obviously lie near $(s\pi/p+1)$ and we therefore write for the solution of Γ

$$\Gamma_s = \frac{s\pi}{p+1} + \Delta\Gamma_s \quad s = 1, 2, \cdots, p \tag{26}$$

$\Delta\Gamma_s$ is a small quantity whose value is to be determined by successive approximations. In making this approximation we assume that $(p+1)\Delta\Gamma_s$ is so small that we can replace the sines of the angles by the angles themselves.

The substitution of Eqs. (25) and (26) in Eqs. (23) and (24) and the evaluation of $\Delta\Gamma_s$ and $\Delta\theta_k$ is tedious but straightforward, yielding finally for the pn desired values of θ,

$$\left.\begin{aligned}
\theta_{0s} &= 2\left(\frac{d+d^2}{n}\right)^{1/2}\sin\frac{s\pi}{2(p+1)} \\
s &= 1, 2, \cdots, p \\
(k &= 0) \\
\theta_{ks} &= \frac{k\pi}{n} + (-1)^k\frac{d}{n}\cot\frac{k\pi}{2n}\left[(-1)^k\left(1 + d - \frac{d}{2n} - \frac{d}{p+1}\right)\right. \\
&\qquad \left. - \left(1 + d - \frac{d}{n}\right)\cos\frac{s\pi}{p+1} - (-1)^k\left(\frac{d}{2n} - \frac{d}{p+1}\right)\cos^2\frac{s\pi}{p+1}\right] \\
s &= 1, 2, \cdots, p \\
k &= 1, 2, \cdots, (n-1).
\end{aligned}\right\} \tag{27}$$

The frequencies of the free periods are obtained through the definition

$$A = (-\,mb\lambda)/T + 2 = 2\cos\theta. \tag{16}$$

From this equation we readily obtain

$$\nu_{ks} = \frac{\lambda_{ks}}{2\pi} = \frac{1}{\pi}\sqrt{\frac{T}{mb}}\,\sin\frac{\theta_{ks}}{2}\,. \tag{28}$$

V. Solution for Two Groups Coupled Together

The solution for the free periods of a system consisting of only two groups coupled together is of some interest, since the solutions can be obtained quite as directly as in the case of a single group, and can as readily be carried to any desired degree of accuracy. We shall therefore consider two cases in which there are only two groups present.

(A) Two groups coupled together and to fixed supports.

In this case in which we have two groups coupled together and to fixed supports we obtain from Eq. (5)

$$F_2 = D_n{}^2(d, d) - d^2 D_{n-1}{}^2(1, d). \tag{29}$$

The condition for a solution is, as usual,

$$F_2 = 0.$$

Using Eq. (19), $(d = d')$, and Eq. (15), this expression becomes

$$\begin{aligned}\left[\frac{\sin(n+1)\theta + 2(d-1)\sin n\theta + (d-1)^2\sin(n-1)\theta}{\sin\theta}\right]^2 \\ -\, d^2\left[\frac{\sin n\theta + (d-1)\sin(n-1)\theta}{\sin\theta}\right]^2 = 0.\end{aligned} \tag{30}$$

On transposing, extracting the square root, and using first the + and then the − sign, we obtain the two following equations

$$\frac{\sin(n+1)\theta + (d-2)\sin n\theta - (d-1)\sin(n-1)\theta}{\sin\theta} = 0 \tag{31}$$

$$\frac{\sin(n+1)\theta + (3d-2)\sin n\theta + (2d^2 - 3d + 1)\sin(n-1)\theta}{\sin\theta} = 0 \tag{32}$$

The solution of these equations can be carried to as high a degree of approximation as is necessary, for any values of the coupling coefficient, d, whatever.

(B) Two groups coupled together, but with free ends.

We may also readily obtain the free periods of a system consisting of two groups of n particles each coupled together but with free ends. This means that $d = 0$ at the 1st and $2n$th particles. The determinantal equation is obtained from Eq. (5) written for only two groups when the terminal elements B of the principal diagonal are replaced by B' where

$$B' = A - 1.$$

Let us call this determinant F_2'. With the aid of these definitions we obtain by expansion as before, see Eqs. (6), (7) and (9),

$$F_2' = D_n^2(d, 0) + d^2 D_{n-1}^2(1, 0).$$

The condition for a solution is, as usual,

$$F_2' = 0.$$

With the aid of Eq. (19) this becomes

$$\frac{\sin (n+1)\theta + (d-2) \sin n\theta - (d-1) \sin (n-1)\theta}{\sin \theta} = \pm d \frac{\sin n\theta - \sin (n-1)\theta}{\sin \theta} \tag{33}$$

On expanding the multiple angles and collecting we have

$$\frac{2 \sin n\theta(\cos \theta - 1)}{\sin \theta} = 0 \tag{34}$$

and

$$\tan n\theta = \frac{d}{1-d} \cot \frac{\theta}{2} \cdot \tag{35}$$

From Eq. (34) we have

$$\theta = \frac{k\pi}{n}, \quad k = 0, 1, 2 \cdots (n-1) \tag{36}$$

The n roots of Eq. (35) must be approximated.

It is interesting to note that if $d = \frac{1}{2}$, Eq. (35) also becomes capable of exact solution, the roots being given by

$$\theta = \frac{2k+1}{2n+1}\pi, \quad k = 0, 1, 2, \cdots, (n-1)\dagger \tag{37}$$

We obtain the free periods by means of our fundamental definition given in Eq. (16), $A(\lambda) = 2 \cos\theta$.

VI. Discussion

A discussion of the results obtained here is most readily undertaken with the aid of a specific example. We have therefore represented in Fig. 2 the free periods which may be obtained from a group of 9 particles under the various arrangements discussed in this paper. For convenience the factor $(1/\pi)(T/mb)^{1/2}$ has been taken equal to unity. When we have the 9 particles

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† Here again the value $k = n$, giving $\theta = \pi$, must be rejected due to the vanishing of the denominator in Eq. (33).

arranged in a uniform group and coupled to a supporting wall with a coupling coefficient $d=1$, we have the frequencies given by the well known formula. Eq. (17), as is shown in case (a). When the coupling coefficient between the group and the support is reduced to $d=0.1$, each of the previous frequencies is decreased, the slower ones more than the faster ones, as is illustrated in case (b). This slowing up of the frequencies with decreasing d is continued until, when $d=0$, the slowest frequency has become zero itself, see case (c). Now let the 9 particles be rearranged into 3 groups of 3 particles each, with a coupling coefficient $d=0.1$ between each group and between the end groups and the supporting walls. The 9 frequencies present rearrange themselves into three sharply defined groups of three frequencies each, see case (d). The number of groups of frequencies present is determined by the number of particles present in each group, that is by the internal structure of the groups under consideration. On the other hand the number of separate frequencies present in each group of frequencies is determined by the total number of groups present in the system. In case (e) we have plotted the frequencies due to three particles arranged in a single group with coupling coefficient $d=0.1$. The dotted lines in case (e) represent the frequencies which would be present if $d=0$. Similarly in case (f) we have plotted the frequencies which would present if each group of case (d) vibrated as a rigid whole. We may speak of these frequencies as the "unmodified group vibrations" of such a system as that shown in case (d). Similarly the two higher frequencies of case (e) may be spoken of as the "unmodified internal vibrations." We may therefore say that the effect of rearranging a single group of pn particles into p groups of n particles each is to rearrange the pn free periods of the original group into n distinct groups of p frequencies each. Or, the effect of coupling together p originally independent groups of n particles each is to slightly modify the p slow group vibrations which would be present if each group vibrated as a rigid whole, and to split each of the $(n-1)$ internal vibrations into p separate components.

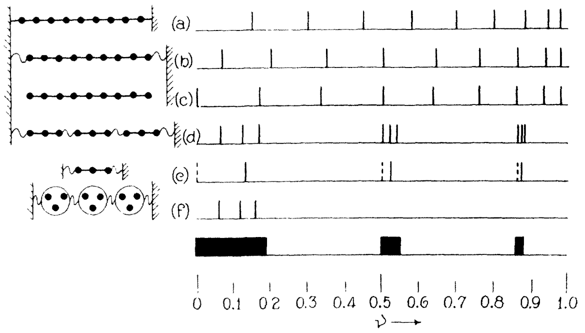

Fig. 2. The free periods obtained from various arrangements of a system conconsisting of 9 massive particles; $1/\pi \cdot T/mb^{1/2}=1$

When the number of groups present has become infinite, as will be true for all practical purposes in any physical crystal, the number of frequencies present in any one group becomes infinite and we have bands instead of groups, see case (g). The lower limit of each band is determined solely by the corresponding "unmodified" frequency of a single group with coupling coefficient $d=0$. See the dotted lines in case (e), Fig. 2. The upper limit, for any given band, is determined solely by the values of d and n, if $p=\infty$. The first and slowest band corresponds to the well-known Debye spectrum of group vibrations, but with a slightly modified upper limit.

Let us now inquire as to the distribution of the individual frequencies within these groups when p has become large but not infinite. To do this we form $(\partial\nu_{ks}/\partial s)$. From Eq. (28) we get

$$\frac{\partial\nu_{ks}}{\partial s}=\frac{1}{2\pi}\left(\frac{T}{mb}\right)^{1/2}\cos\frac{\theta_{ks}}{2}\frac{\partial\theta_{ks}}{\partial s}\cdot$$

It is evident that the frequencies will be closest together, that is to say the density of lines in the elastic spectrum will be greatest, when $(\partial\nu_{ks}/\partial s)$ is a minimum. An investigation of the above expression with the aid of Eqs. (27) shows that, to a first approximation, the frequencies of the group, or Debye, vibrations crowd together or converge toward the high frequency limit of the group. The grouping of the frequencies is exactly analogous to that holding in cases (a), (b), and (c) of Fig. 2. In the case of the internal vibrations, to a first approximation, the frequencies converge toward both the high and low frequency limits of the group. The lines here have their minimum density at the center of the group.

It is not to be inferred from the preceding discussion of frequencies and bands that each of the frequencies predicted by Eqs. (27) can be expected to appear in the optical spectrum of the corresponding compound. The question of the optical activity of a given frequency is essentially a question concerning the electric moment of the molecule. It is hoped that an investigation of this question can be made at a later date.

VII. Application to the Specific Heats of Organic Compounds

Although it is not the purpose of this paper to discuss in detail the applications of the equations just derived, an obvious example will be given. If we have, by any means, an approximate value for the forces of restitution acting upon an atom in a crystal of an organic chain compound, we have here the means for computing its free periods. By applying the proper Debye or Einstein functions we can then compute its specific heat as a function of temperature. The frequencies arising from the terms containing θ_{0s}, being molecular vibrations, will give rise to a Debye term. It is necessary then to know only the upper limit of the terms defined by θ_{0s}, that is θ_{0p}. When p becomes large this term becomes $\theta_{0p}=2(d+d^2/n).^{1/2}$ For the internal vibrations it will in general suffice to neglect the correction terms in Eqs. (27) and write $\theta_{ks}=k\pi/n$. In case the frequency band is unusually wide, as will be the case with the "internal" bands of hexyl alcohol, we may use the average frequency of the band in the specific heat formula. Even in this case the correction is practically negligible.

For the force of restitution due to a displacement along the length of the molecular chain we will take 4×10^5 dynes/cm. This force will give a band in the neighborhood of 28μ for all our compounds. For the force of restitution due to a displacement perpendicular to the length of the chain we will take 0.12×10^5 dynes/cm. This value has been chosen more or less arbitrarily to fit the data. It is, however, of the same order of magnitude as the corresponding constants proposed by Andrews[5,14] which range from 0.32 to 0.66×10^5 dynes/cm. It is to be noted that these constants are not forces of restitution due to a displacement along or perpendicular to the length of the valence bond itself, but are precisely as stated forces due to a displacement along or perpendicular to the length of the entire chain. The vibration of hydrogen against carbon has been neglected since others have shown that its effect is negligible.[6]

There seems to be no reliable method for computing the forces acting between the molecules in organic crystals. The Lindemann formula[15] is strictly applicable to monatomic crystals, and Andrew's modification of it[6] is of doubtful service here because of the high lack of symmetry of the chain molecules. The intermolecular forces have, therefore, been chosen arbitrarily. At low temperatures, 20°K, the internal vibrations have for the most part ceased to contribute to the specific heat. A Debye function has therefore been chosen to fit the data at this point. From the value of ν_0 so chosen it is possible to compute the corresponding force constant and the coupling coefficient *d*. This has been done.

The Debye function has been computed for three degrees of freedom, which assumes an isotropic crystal. The Einstein functions arising from the internal vibrations have been taken as having two degrees of freedom when the motion is perpendicular to the length of the chain, and one degree of freedom when along the length of the chain. The heat absorbed due to the expansion of the crystal has been computed according to Andrew's modification of Nernst's formula[6]

$$C_p - C_v = (C_v^2)_{\text{molecule}} \times \frac{T}{T_m} \times 0.0214$$

where $(C_v)_{\text{molecules}}$ is the specific heat at constant volume arising from the Debye terms alone, T is the temperature at which computations are being made and T_m is the melting point of the crystal under investigation.

Specific heat data are available for four of the normal alcohols. The computations have therefore been carried through for these substances. The frequencies found, neglecting the correction terms, as well as the total band width to be expected, expressed as percent of the corresponding uncorrected frequency, are summarized in Table I. In this table ν_0 represents the upper

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[14] J. R. Bates and D. H. Andrews, Proc. Nat. Acad. Sci. (U.S.A.), **14,** No. 2, 124 (1928), D. H. Andrews, Phys. Rev. **34,** 1626 (1929).

[15] F. A. Lindemann, Phys. Zeits. **11,** 609 (1910).

limit of the Debye terms, chosen arbitrarily to fit the data as stated above. The other frequencies, ν_1, ν_2, etc., represent the internal vibrations. The frequency bands, of width given by $\Delta\nu$, will always extend towards higher frequencies from the uncorrected frequency given in the table.

TABLE I.

	$10^{-11}\times$	ν_0	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Methyl Alcohol	(Trans)	29	48					
	(Long)		277					
$\Delta\nu$ in %			0.6					
Ethyl Alcohol	(Trans)	25	35	60				
	(Long)		200	347				
$\Delta\nu$ in %			1.2	0.7				
Butyl Alcohol	(Trans)	48	22	41	57	67		
	(Long)		126	239	329	387		
$\Delta\nu$ in %			16	2.8	0.8	0.1		
Hexy Alcohol	(Trans)	48	16	32	44	55	64	69
	(Long)		91	177	255	320	370	400
$\Delta\nu$ in %			36	6.4	2.3	1.0	0.4	0.1

Using these frequencies the calculations for ethyl alcohol give the following results, where $3D(\ )$ represents a Debye function with 3 degrees of freedom, $1E(\ )$ represents an Einstein function with 1 degree of freedom. etc.

TABLE II. *Ethyl alcohol, $n=3$.*

T°K	30	60	90	150
$3D(120/T)$	3.0	4.9	5.5	5.8
$1E\,(959/T)$	—	—	—	0.1
$1E\,(1660/T)$	—	—	—	—
$2E\,(166/T)$	0.5	2.2	3.0	3.6
$2E\,(288/T)$	—	0.8	1.8	2.9
C_v corr.	—	0.2	0.4	0.7
Total C_p, Cal/Mol	3.5	8.0	10.6	13.1

The computations for the other alcohols have been carried through and are plotted in Fig. 3, in which the solid lines represent the curves computed in the manner just indicated and the plotted points the observed values given by the authors indicated.

From the Debye functions chosen to fit the data at low temperatures we get values of ν_0 which give us values for the constant d for each substance in the manner indicated above. The results are as follows:

TABLE III.

Substance	No. groups	d
Methyl Alcohol	2	0.011
Ethyl Alcohol	3	0.012
Butyl Alcohol	5	0.070
Hexyl Alcohol	7	0.096

With the exception of ethyl alcohol the coupling coefficient varies approximately as the number of groups in the molecule. The low value of the coupling coefficient in the case of ethyl alcohol may have significance when considered in connection with the ease with which this substance forms glasses at low temperatures.

The agreement of the computed values with the observed values is as close as is to be expected, considering the very approximate nature of the calculations. There are, to be sure, no reasons for believing that these organic crystals are actually isotropic as has been assumed. Neither can we be particularly certain about the correction applied according to Nernst's formula for the conversion of C_v into C_p. The value of the constant 0.0214 was chosen originally to fit the data obtained in the case of certain metals and halogen salts,[16] and we have no *apriori* reason for applying it directly to the case of organic crystals. Moreover these compounds have been treated as though each molecule was a uniformly loaded string which is actually not the case. The mass of the OH group is actually 17 as against 14 for the CH_2 group and 15 for the CH_3 group.

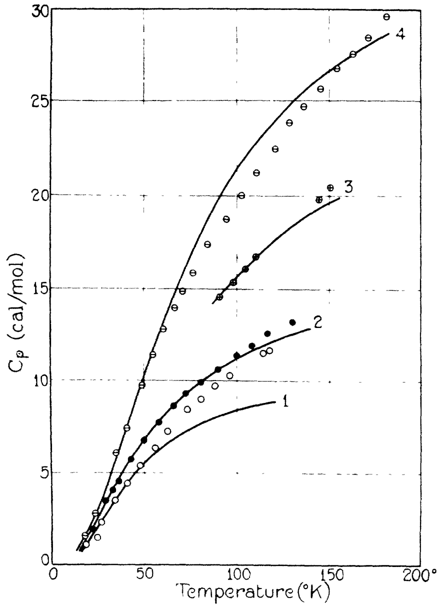

Fig. 3. C_p in cal/mol for the normal alcohols. (1) Methyl Alcohol K. K. Kelley, J. Amer. Chem. Soc. **51,** 180 (1929), (2) Ethyl Alcohol K. K. Kelley, J. Amer. Chem. Soc. **51,** 779 (1929), (3) Butyl Alcohol G. S. Parks, J. Amer. Chem. Soc. **47,** 338 (1925). (4) Hexyl Alcohol K. K. Kelley, J. Amer. Chem. Soc. **51,** 779 (1929).

An additional remark should be made concerning the frequencies given in Table I. The values given under ν_0, the upper limit of the Debye frequencies, have been chosen, as stated, to fit the data at 20°K and, so far as the comput-

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[16] W. Nernst and F. A. Lindemann, Zeit. f. Elektrochemie **17,** 818 (1911).

ations are concerned, may be looked upon as arbitrary constants. From these values of ν_0 values have been obtained for d which justify the original assumption that d is a small quantity. In the same way the absolute values of the frequencies of the internal vibrations are arbitrary, since the constant T/b was chosen more or less arbitrarily. These internal frequencies can therefore be considered significant only when taken in the ratio $\nu_1{:}\nu_2{:}\nu_3$ etc., or ν_1 (Methyl) :ν_1(Ethyl) etc. The results of applying Eqs. (27) to the computation of the specific heats of organic crystals are thus largely not characteristic of this paper. That is to say, for reasonable values of d, and within the limits of experimental error, Eqs. (27) indicate that the correction terms in the expressions for ν_{ks} are negligible, and the computation of the internal frequencies reverts to the well-known case of the uniformly loaded string with free ends.

No explanation is offered for the unusually high value of the specific heat of methyl alcohol as compared with the theoretical curve. On the other hand the manner in which the other experimental points have been reproduced by the theoretical curves is taken as evidence of the essential soundness of the underlying assumptions and calculations. If the data were available it would be highly desirable to carry through the corresponding calculations for the higher members of this or some similar series of compounds.

In conclusion the author wishes to acknowledge his indebtedness to Professor D. H. Andrews who originally suggested the problem and who has been most kind in discussing its details. The author is also indebted to Professor F. D. Murnaghan for valuable suggestions in connection with the mathematical treatment. Finally it is a pleasure to acknowledge the continual assistence of Professor K. F. Herzfeld under whose direction this paper was written.