

T2. Vibrational structure of polyynes

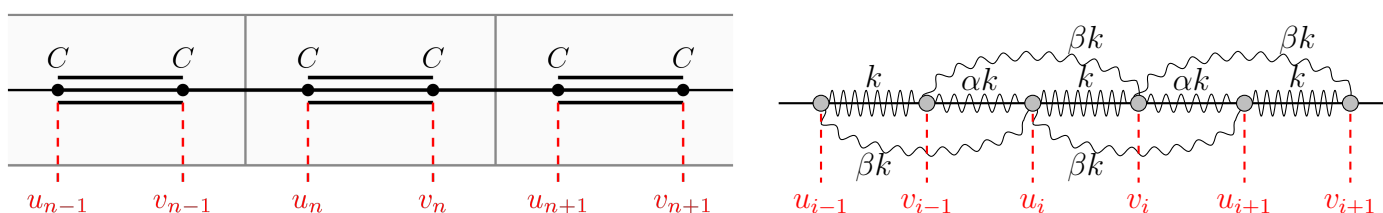
In this problem, you will explore *polyynes* — organic compounds that contain several alternating single and triple bonds between carbon atoms in their structure. You may use the following constants:

- $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$ — Avogadro's number,
- $M_C = 12.0 \text{ g/mol}$ — the molar mass of a carbon atom,
- $\hbar = \frac{h}{2\pi} = 1.055 \cdot 10^{-34} \text{ J} \cdot \text{s}$ — the reduced Planck constant.

Part A. An infinite chain of carbon atoms

First, examine an infinite one-dimensional chain of carbon atoms with alternating single and triple bonds, as shown in the figure. We will describe the system using the ball-and-spring model. Assume that all carbon atoms (balls) have identical masses equal to m , the triple bond corresponds to a spring with spring constant k , the single bond to a spring with constant αk , and additionally, every other atom (ball) is connected by a spring with constant βk (for visualization convenience, such springs are shown in a curved shape in the figure; in reality, all springs are horizontal).

Use the following notation: u_n, v_n — the displacements from equilibrium positions for the left and right atoms (balls), connected by a triple bond, respectively. We will say that two such atoms form a unit cell. Note that index n ranges over all **integer** values.



A1	Write the expression for the total energy of the system. Express your answer in terms of all coordinates u_n, v_n , their first-order time derivatives, as well as the parameters m, k, α, β .
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The time derivative of the system's total energy can be expressed as

$$\dot{E} = \sum_n (A\dot{u}_n + B\dot{v}_n),$$

where A and B are expressions containing u_n, v_n , and their second-order time derivatives. The equations $A = 0$ and $B = 0$ describe the system's motion and turn out to be equivalent to Newton's second law.

Note that an infinite sum of the form

$$\sum_n a_n b_{n-1}$$

can be transformed by “shifting” indices

$$\sum_n a_n b_{n-1} = \sum_n a_{n+1} b_n.$$

A2	Derive the system of differential equations describing the motion of all atoms. Express your answer in terms of coordinates u_n, v_n and their second time derivatives, along with the parameters m, k, α, β .
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To solve such systems of linear differential equations, the method of complex amplitudes is used. This involves seeking solutions in the form of complex functions, while the true solution corresponds to their real (or imaginary) part. In this problem we are interested in solutions that are plane waves

$$u_n(t) = U \cdot \exp(-i\omega t + iqn), \quad v_n(t) = V \cdot \exp(-i\omega t + iqn).$$

A3 Derive a system of linear equations for the coefficients U and V of the form

$$\begin{cases} a \cdot U + b \cdot V = 0, \\ c \cdot U + d \cdot V = 0. \end{cases}$$

Express the coefficients a , b , c , and d in terms of m , k , α , β , ω , and q . You may need Euler's formula

$$\exp(ix) = \cos x + i \sin x.$$

The resulting system of equations necessarily admits the trivial solution $U = V = 0$. However, we are interested in the alternative case when the carbon chain undergoes oscillations. The following fact will be useful: a system of linear equations of this form has a non-trivial solution if and only if the relation $ad - bc = 0$ is satisfied. Importantly, in this case there are infinitely many solutions: they correspond to oscillations of the same form but with different amplitudes. The collective oscillatory motion of the chain's atoms is called a phonon. We say that a phonon "runs" along the chain. The quantity ω is called the frequency, while q is the phonon's quasimomentum.

The phonon dispersion relation (spectrum) refers to the dependence of the phonon frequency ω on its quasimomentum q .

A4 Derive the dispersion relations for the two possible phonons that can propagate in the considered carbon chain. As your answer, specify the ratio ω/ω_0 , where $\omega_0 = \sqrt{k/m}$. The answer (the specified ratio) may only include the parameters α , β and q .

A5 Simplify the dispersion relations found in the previous part for the case $q \rightarrow 0$ by expanding them in a Taylor series about $q = 0$. Your answer should include the first non-zero, non-constant term in the expansion. Use the following approximation formulas: $1 - \cos x \simeq x^2/2$ and $(1 + x)^\gamma \simeq 1 + \gamma x$ for $x \rightarrow 0$.

Phonons for which $\omega(q) \propto q$ as $q \rightarrow 0$ are called **acoustic**; all other phonons are **optical**.

A6 Simplify the dispersion relations obtained in the previous part for the case $q \rightarrow \pi$ by expanding them in a Taylor series with respect to $(q - \pi)$ about 0. Assume that $\alpha < 1$ is known. Your answer should include the first non-zero, non-constant term in the expansion.

A7 Sketch the graph of dispersion curves $\omega(q)$ for $q \in [-\pi, \pi]$ for the following cases:

- $\alpha = 0.5, \beta = 0.1$;
- $\alpha = 0.5, \beta = 3.0$.

Pay attention to the relative arrangement of the curves, their behavior near the points $q = 0$ and $q = \pi$ and possible extrema.

Part B. Spectroscopy of polyynes

The model discussed in Part A of the problem provides a reasonably accurate description of **polyynes** — the organic compounds that will be discussed further. It is important to note that, unlike the model in Part A, real molecules have a finite length, which affects their phonon spectrum.

Let us consider the same chain as in Part A, but of finite length. Suppose it consists of $N + 1$ unit cells. In other words, the index n takes all integer values from 0 to N . Assume both ends of the chain are fixed, i. e., the displacements $u_0 = u_N = v_0 = v_N = 0$ at any moment in time.

In the infinite chain model, solutions were found in the form of traveling plane waves. Since the dynamics of such a system is described by a system of linear equations, any linear combination of solutions is also its solution. In other words, if the sets of functions u_n, v_n and $\tilde{u}_n, \tilde{v}_n$ are solutions, then the set of functions $\mu u_n + \eta \tilde{u}_n, \mu v_n + \eta \tilde{v}_n$ (μ, η are arbitrary complex numbers) also satisfies the system of equations describing the system's dynamics.

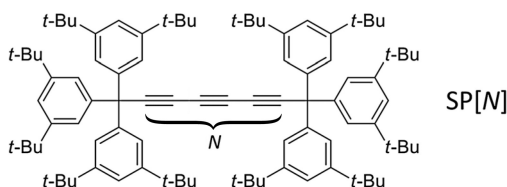
Consider a linear combination with coefficients μ and η of two plane waves propagating in opposite directions in the chain (i.e., with quasimomenta q and $-q$).

B1	Apply the boundary conditions for the finite chain with $N + 1$ unit cells and obtain a system of two linear equations for μ and η . The coefficients in the equation may depend only on the quantities q and N .
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The linear combination with coefficients μ and η satisfying the derived system represents a solution to the dynamics equations describing the finite chain with the specified boundary conditions.

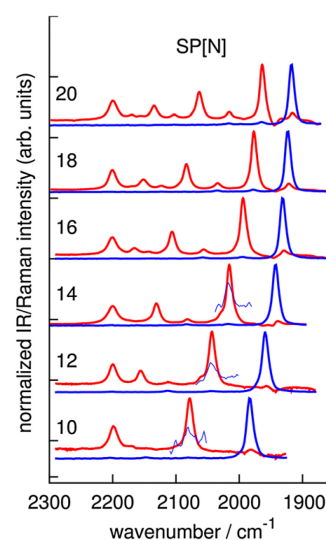
B2	For what values q_l of quasimomentum the system has a nontrivial solution? Express the answer in terms of N and integer number l .
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In the early 2010s, Canadian scientists from the University of Alberta, Wesley A. Chalifoux and Rik R. Tykwinski, developed a method to synthesize symmetric endcapped polyynes $SP[N]$, where N denotes the number of triple bonds in the carbon chain. The molecular structure is shown in the figure.



The physical meaning of the end groups is that they determine the boundary conditions. The specified end groups allow us to consider both ends of the chain (atoms bonded to four neighbors) as fixed. As you saw in questions B1–B2, the finite size of the chain and the introduction of boundary conditions result in only discrete resonances being observed in the phonon spectrum.

The positions of resonances could be determined experimentally using IR and Raman spectroscopy — methods based on light-matter interaction. For $SP[N]$ polyynes with different numbers N of triple bonds, the energies of phonons that can arise in the molecule are measured. The figure shows the phonon spectrum: red color indicates results obtained by IR spectroscopy, while blue represents Raman spectroscopy data. The excitation of the low-energy optical phonon corresponds to the far-right intensity peak (in all cases shown in the figure, it appears as “blue”). The phonon energy E is



related to its frequency ω by the formula $E = \hbar\omega$. Note: the horizontal axis shows energy in inverse centimeters. Use the following conversion formula to obtain energy in Joules:

$$1 \text{ cm}^{-1} = 1.99 \cdot 10^{-23} \text{ J}.$$

Since only one atom is fixed rather than an entire unit cell as in questions B1-B2, we need to use the following approach to describe the system. We imaginarily add one carbon atom to each end of the chain, bonded to the terminal atoms via triple bonds, and fix the terminal unit cells. This results in a chain consisting of $N + 2$ unit cells with fixed ends.

Since the number N in the experimentally studied chains is sufficiently large, the distant coupling (βk) at the very edge, which appeared after the described approach, has practically no effect on the phonon spectrum.

B3	Using the value $\beta = 3.0$ and the experimental results (only the rightmost peak), determine the spring constants of the single and triple bonds. Assume it is known that for the parameters α and β realized in the experiment, the dispersion relation $\omega(q)$ is an increasing function on the interval $(0; \pi)$.
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The carbon chains you were asked to investigate are of scientific interest as they can be used in molecular electronics. The problem incorporates experimental results published in the article: Agarwal, N.R., Lucotti, A., Fazzi, D., Tommasini, M., Castiglioni, C., Chalifoux, W.A. and Tykwinski, R.R. (2013), Structure and chain polarization of long polyynes investigated with infrared and Raman spectroscopy. *J. Raman Spectrosc.*, 44: 1398-1410.

Solution

A1. The full energy consists of the potential energy of deformed springs and the kinetic energy of atomic motion, so

$$E = \sum_n \left(\frac{k(u_n - v_n)^2}{2} + \frac{\alpha k(u_{n+1} - v_n)^2}{2} + \frac{\beta k(u_{n+1} - u_n)^2}{2} + \frac{\beta k(v_{n+1} - v_n)^2}{2} + \frac{m\dot{u}_n^2}{2} + \frac{m\dot{v}_n^2}{2} \right)$$

A2. Differentiating the energy expression, we obtain

$$\begin{aligned} \dot{E} = \sum_n & \left(k(u_n - v_n)(\dot{u}_n - \dot{v}_n) + \alpha k(u_{n+1} - v_n)(\dot{u}_{n+1} - \dot{v}_n) + \beta k(u_{n+1} - u_n)(\dot{u}_{n+1} - \dot{u}_n) \right. \\ & \left. + \beta k(v_{n+1} - v_n)(\dot{v}_{n+1} - \dot{v}_n) + m\dot{u}_n\ddot{u}_n + m\dot{v}_n\ddot{v}_n \right). \end{aligned}$$

Grouping the terms containing $\dot{v}_n$ and $\dot{u}_n$

$$\begin{aligned} \dot{E} = \sum_n & \left(\dot{v}_n(m\ddot{v}_n + kv_n(\alpha + 1 + 2\beta) - ku_n - \alpha ku_{n+1} - \beta k(v_{n-1} + v_{n+1})) \right. \\ & \left. + \dot{u}_n(m\ddot{u}_n + ku_n(\alpha + 1 + 2\beta) - kv_n - \alpha kv_{n-1} - \beta k(u_{n-1} + u_{n+1})) \right). \end{aligned}$$

Here we used that

$$\sum_n \dot{v}_{n+1}(v_{n+1} - v_n) = \sum_n \dot{v}_n(v_n - v_{n-1}), \quad \sum_n \dot{u}_{n+1}(u_{n+1} - v_n) = \sum_n \dot{u}_n(u_n - v_{n-1}),$$

and

$$\sum_n \dot{u}_{n+1}(u_{n+1} - u_n) = \sum_n \dot{u}_n(u_n - u_{n-1}).$$

Setting the coefficients A and B to zero leads to the system of differential equations.

$$\begin{cases} m\ddot{v}_n + kv_n(\alpha + 1 + 2\beta) - ku_n - \alpha ku_{n+1} - \beta k(v_{n-1} + v_{n+1}) = 0, \\ m\ddot{u}_n + ku_n(\alpha + 1 + 2\beta) - kv_n - \alpha kv_{n-1} - \beta k(u_{n-1} + u_{n+1}) = 0. \end{cases}$$

We recognize that the derived equations describe Newtonian dynamics of the two atoms in the unit cell.

A3. Using $u_n(t) = U \cdot \exp(-i\omega t + iqn)$, $v_n(t) = V \cdot \exp(-i\omega t + iqn)$ we obtain expressions for the second time derivatives of the displacements

$$\ddot{u}_n(t) = -\omega^2 U \cdot \exp(-i\omega t + iqn), \quad \ddot{v}_n(t) = -\omega^2 V \cdot \exp(-i\omega t + iqn).$$

Substituting these expressions into system from A2 and dividing by $\exp(-i\omega t + iqn)$. We obtain

$$\begin{cases} -\omega^2 mV + kV(\alpha + 1 + 2\beta) - kU - \alpha kU \exp(iq) - \beta kV(\exp(-iq) + \exp(iq)) = 0, \\ -\omega^2 mU + kU(\alpha + 1 + 2\beta) - kV - \alpha kV \exp(-iq) - \beta kU(\exp(-iq) + \exp(iq)) = 0. \end{cases}$$

After regrouping the terms, the system takes the required form

$$\begin{cases} k(1 + \alpha \exp(iq)) \cdot U + (\omega^2 m - k(\alpha + 1 + 2\beta) + \beta k(\exp(-iq) + \exp(iq))) \cdot V = 0, \\ (\omega^2 m - k(\alpha + 1 + 2\beta) + \beta k(\exp(-iq) + \exp(iq))) \cdot U + k(1 + \alpha \exp(iq)) \cdot V = 0. \end{cases}$$

Using Euler's formula, we find that $\exp(-iq) + \exp(iq) = 2 \cos q$. The system transforms to

$$\begin{cases} k(1 + \alpha \exp(iq)) \cdot U + (\omega^2 m - k(\alpha + 1 + 2\beta) + 2\beta k \cos q) \cdot V = 0, \\ (\omega^2 m - k(\alpha + 1 + 2\beta) + 2\beta k \cos q) \cdot U + k(1 + \alpha \exp(-iq)) \cdot V = 0. \end{cases}$$

A4. If a phonon can propagate in the chain, then non-trivial solutions to system A3 exist which implies the condition $ad - bc = 0$. Therefore

$$k^2(1 + \alpha \exp(iq))(1 + \alpha \exp(-iq)) = (\omega^2 m - k(\alpha + 1 + 2\beta) + 2\beta k \cos q)^2.$$

The direct consequence of Euler's formula is

$$(1 + \alpha \exp(iq))(1 + \alpha \exp(-iq)) = 1 + \alpha^2 + \alpha(\exp(iq) + \exp(-iq)) = 1 + 2\alpha \cos q + \alpha^2.$$

Substitute this into the original equation and divide by k^2 , hence we obtain

$$1 + 2\alpha \cos q + \alpha^2 = \left(\frac{\omega^2}{\omega_0^2} - (\alpha + 1 + 2\beta) + 2\beta \cos q \right)^2.$$

Therefore

$$\pm \sqrt{1 + 2\alpha \cos q + \alpha^2} = \frac{\omega^2}{\omega_0^2} - (\alpha + 1 + 2\beta) + 2\beta \cos q,$$

and the dispersion relation takes the form

$$\frac{\omega}{\omega_0} = \sqrt{\pm \sqrt{1 + 2\alpha \cos q + \alpha^2} - 2\beta \cos q + \alpha + 1 + 2\beta}$$

A5. For $q \rightarrow 0$ the approximation $\cos q \simeq 1 - \frac{q^2}{2}$ holds. The dispersion relation takes the form

$$\frac{\omega}{\omega_0} \simeq \sqrt{\pm \sqrt{1 + 2\alpha - \alpha q^2 + \alpha^2} + \beta q^2 + \alpha + 1} = \sqrt{(1 + \alpha) \left(\pm \sqrt{1 - \frac{\alpha q^2}{(1 + \alpha)^2} + \frac{\beta q^2}{1 + \alpha} + 1} \right)}.$$

Expanding the square root in a Taylor series

$$\frac{\omega}{\omega_0} \simeq \sqrt{(1 + \alpha) \left(\pm \left(1 - \frac{\alpha q^2}{2(1 + \alpha)^2} \right) + \frac{\beta q^2}{1 + \alpha} + 1 \right)}.$$

Next, we examine the first phonon solution

$$\left(\frac{\omega}{\omega_0} \right)_1 \simeq \sqrt{\frac{\alpha q^2}{2(1 + \alpha)} + \beta q^2}.$$

$$\left(\frac{\omega}{\omega_0} \right)_1 \simeq |q| \sqrt{\frac{\alpha}{2(1 + \alpha)} + \beta}$$

For the second phonon

$$\frac{\omega}{\omega_0} \simeq \sqrt{2(1 + \alpha) \left(1 - \frac{\alpha q^2}{4(1 + \alpha)^2} + \frac{\beta q^2}{2(1 + \alpha)} \right)}.$$

Again, we expand the square root in a Taylor series

$$\left(\frac{\omega}{\omega_0}\right)_2 \simeq \sqrt{2(1+\alpha)} \left(1 + \frac{1}{4} \left(\frac{\beta}{1+\alpha} - \frac{\alpha}{2(1+\alpha)^2}\right) q^2\right)$$

A6. Using the variable $p = q - \pi$. The dispersion relation takes the form

$$\frac{\omega}{\omega_0} \simeq \sqrt{\alpha + 1 + 4\beta - \beta p^2 \pm \sqrt{1 - 2\alpha + \alpha p^2 + \alpha^2}} = \sqrt{\alpha + 1 + 4\beta - \beta p^2 \pm (1 - \alpha)} \sqrt{1 + \frac{\alpha p^2}{(1 - \alpha)^2}}.$$

Therefore, for the acoustic phonon

$$\frac{\omega}{\omega_0} \simeq \sqrt{2\alpha + 4\beta - \left(\beta + \frac{\alpha}{2(1-\alpha)}\right) p^2} = \sqrt{2\alpha + 4\beta} \sqrt{1 - \frac{1}{2(\alpha + 2\beta)} \left(\beta + \frac{\alpha}{2(1-\alpha)}\right) p^2}.$$

Again, we expand the square root in a Taylor series

$$\left(\frac{\omega}{\omega_0}\right)_1 \simeq \sqrt{2\alpha + 4\beta} \left(1 - \frac{1}{4(\alpha + 2\beta)} \left(\beta + \frac{\alpha}{2(1-\alpha)}\right) p^2\right)$$

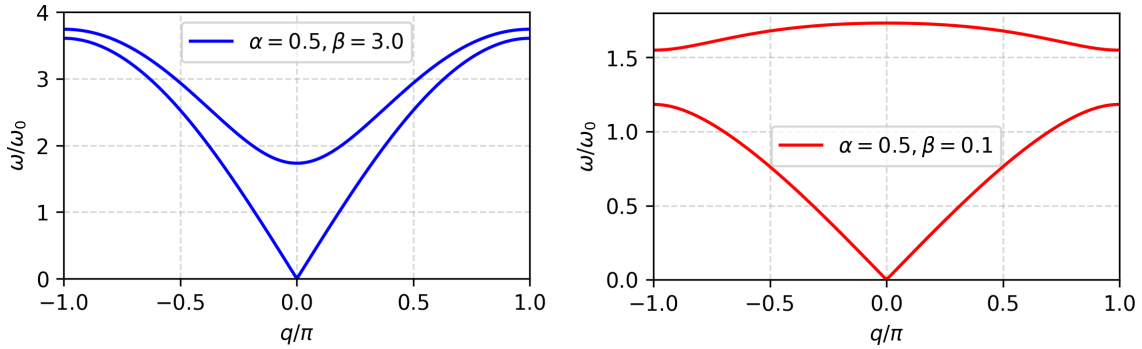
For the optical phonon:

$$\frac{\omega}{\omega_0} \simeq \sqrt{2 + 4\beta - \left(\beta - \frac{\alpha}{2(1-\alpha)}\right) p^2} \simeq \sqrt{2 + 4\beta} \sqrt{1 - \frac{1}{2(1 + 2\beta)} \left(\beta - \frac{\alpha}{2(1-\alpha)}\right) p^2}.$$

Again, we expand the square root in a Taylor series

$$\left(\frac{\omega}{\omega_0}\right)_2 \simeq \sqrt{2 + 4\beta} \left(1 - \frac{1}{4(1 + 2\beta)} \left(\beta - \frac{\alpha}{2(1-\alpha)}\right) p^2\right)$$

A7.



B1. Substituting the solutions in the form of plane waves, we obtain

$$u_n^\Sigma = \mu u_n + \eta \tilde{u}_n = U \exp(-i\omega t) (\mu \exp(iqn) + \eta \exp(-iqn)),$$

and similarly

$$v_n^\Sigma = \mu v_n + \eta \tilde{v}_n = V \exp(-i\omega t) (\mu \exp(iqn) + \eta \exp(-iqn)).$$

The conditions $u_0^\Sigma = 0$ and $v_0^\Sigma = 0$ turn out to be equivalent to each other, just as the conditions $u_N^\Sigma = 0$ and $v_N^\Sigma = 0$ are. Thus,

$$\begin{cases} \mu + \eta = 0, \\ \mu \exp(iqN) + \eta \exp(-iqN) = 0. \end{cases}$$

B2. To answer this question, one can use the technique described in part A of this problem. However, it is simpler to substitute $\eta = -\mu$ from the first equation into the second and divide by μ , taking into account the existence of a nontrivial solution. We obtain $\exp(iqN) = \exp(-iqN)$, which is equivalent to $\exp(2iqN) = 1$, i.e., $2qN = 2\pi l$, $l \in \mathbb{Z}$. Note that at $q = 0$ the phonon amplitude becomes zero, so $l = 0$ must be excluded from the answer.

$$q = \frac{\pi l}{N}, \quad l \in \mathbb{Z}, l \neq 0$$

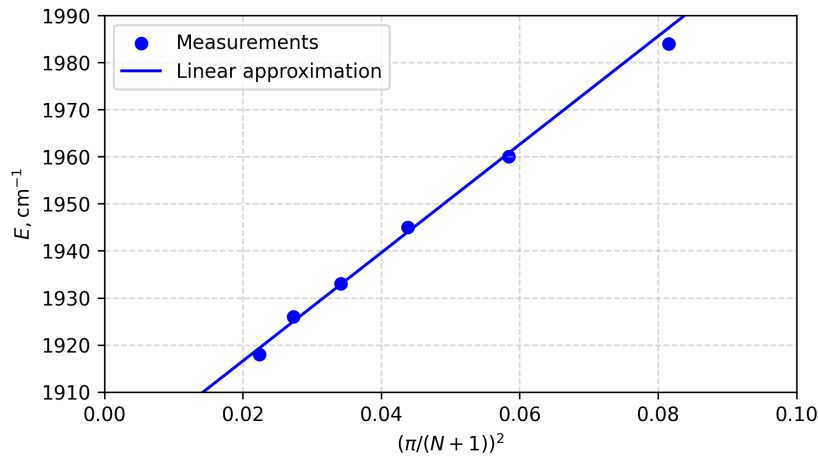
B3. From the condition, it follows that the quasimomentum q can be expressed as $q = \frac{\pi l}{N+1}$, $l \in \mathbb{Z}$ (since after applying the described technique, the chain contains $N + 2$ unit cells). The low-energy phonon corresponds to the minimum absolute value of quasimomentum, i.e., $q = \frac{\pi}{N+1}$.

Using the provided experimental plot, we extract the dependence of the low-energy phonon's energy on N . We employ the Taylor series expansion of ω/ω_0 near the point $q = 0$. Thus,

$$\frac{\omega}{\omega_0} \simeq \sqrt{2(1+\alpha)} \left(1 + \left(\frac{\beta}{4(1+\alpha)} - \frac{\alpha}{8(\alpha+1)^2} \right) \left(\frac{\pi}{N+1} \right)^2 \right).$$

N	$E, \text{ cm}^{-1}$	$\pi^2/(N+1)^2$
20	1918	0.0224
18	1926	0.0273
16	1933	0.0341
14	1945	0.0439
12	1960	0.0584
10	1984	0.0816

Let's plot the dependence $E(x = (\pi/(N+1))^2)$. As theoretically expected, it turned out to be linear. From the plot, we find the equation of the approximating line $E = (1150x + 1900) (\text{cm}^{-1})$.



From the above, we obtain the system of equations

$$\begin{cases} 1150 \text{ cm}^{-1} = \hbar\omega_0 \sqrt{2(1+\alpha)} \left(\frac{\beta}{4(1+\alpha)} - \frac{\alpha}{8(\alpha+1)^2} \right), \\ 1900 \text{ cm}^{-1} = \hbar\omega_0 \sqrt{2(1+\alpha)}. \end{cases}$$

Solving this system yields

$$\alpha = 0.204, \quad \omega_0 = 2.31 \cdot 10^{14} \text{ s}^{-1}.$$

Given that $\omega_0 = \sqrt{\frac{k}{m}}$, we find

$$k = \omega_0^2 m = 1.06 \cdot 10^3 \text{ N/m}.$$

$$\alpha k = 216 \text{ N/m}, \quad k = 1.06 \cdot 10^3 \text{ N/m}$$