

Stationary energy partition between modes in the one-dimensional carbyne chain

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Abstract

The stationary patterns of energy partition between waves in a one-dimensional carbyne chain at ambient temperatures are investigated, taking into account central and noncentral interactions between carbon atoms. The study is carried out by standard asymptotic methods of nonlinear dynamics in the framework of classical mechanics, based on a simple mathematical model. Within the first-order nonlinear approximation analysis the triple-phonon resonant ensembles of quasi-harmonic waves are revealed. Each resonant triad consists of a single primary high-frequency longitudinal mode and a pair of secondary low-frequency transverse modes of oscillations. In general, the carbyne chain is described as a superposition of resonant triads of various spectral scales. It is found that the stationary energy distribution in a carbyne is obeyed to the classical Rayleigh-Jeans law, with the allowances for the proportional amplitude dispersion, which influences upon the results of theoretical estimations in several percents, comparing to the linear theory prediction.

1 Introduction

Carbyne, a one-dimensional carbon allotrope, has been first found and studied in the early sixties of the last century [1]. This is a natural material, since its presence had been detected in meteorites [2]. Carbyne is of particular interest for nanotechnology, being the most hard of all known materials [3] up today, strongly than a diamond. At the same time, the specific heat capacity of carbyne is larger than the heat capacity of graphite, and the latter is higher than a diamond. This ordering is due to the spatial framework of these carbon allotropes [1]. The flexibility of carbyne has approximately the same order as most polymers, though this can be efficiently controlled by attaching to the ends of a chain some chemicals [3]. In this case, the carbyne chain can be turned from a random coil, with the persistent length of order 14 [nm], into a strong string of extremely small diameter and extremely large value of the Young's modulus. The bending of carbyne chains is resulted in an additional voltage between the carbon atoms to exhibit the semiconducting properties. This feature can be utilized in NEMS as a precision sensor. In addition to the strength properties, carbyne displays a number of other unique properties, opening prospects for the using in hydrogen storage technologies to produce ecologically

friendly batteries. These unique properties stimulate an intensive discussion over the synthesizing a carbyne from a liquid carbon [4, 5, 6].

Based on a most simple mathematical model of a carbyne chain, the three-wave resonances are investigated, which arise due to the nonlinear coupling between central and noncentral bonds of nearest neighborhood carbon atoms. It is shown that the low-frequency longitudinal waves are almost always unstable. These break up into pairs of secondary low-frequency transverse waves, unless the frequency of the primary longitudinal mode does not exceed a certain critical value. Otherwise, the three-wave resonant processes are forbidden, and the standard Rayleigh–Jeans law holds true, prescribing an equal energy partition among degrees of freedom. Thus, for the short-wave processes, the stationary pattern of energy distribution between waves is highly simplified. It is found that the law of stationary energy partition in a carbyne chain at room temperature is close, within the high-frequency spectral band, to the Rayleigh–Jeans law. Some differences arise due to the presence of triple-wave resonant processes at low-frequency vibrations. This can affect the specific heat, thermal conductivity and other phenomenological parameters of the system, especially at low temperatures.

2 Mathematical model

We consider mechanical vibrations of a simple one-dimensional chain consisting of particles of equal masses m , at equal distances a . Each particle has two degrees of freedom on the plane of oscillation. The forces between the particles are both central and noncentral. Accounting for noncentral forces leads to appearance of the so-called *bending* oscillatory modes. An absolute elongation of a segment in the chain λ_n , and the curvature of the median line κ_n , in the vicinity of the atom number n can be expressed as it follows:

$$\lambda_n = \sqrt{(a + (u_n - u_{n-1}))^2 + (w_n - w_{n-1})^2} - a;$$

$$\kappa_n = \arctan\left(\frac{w_n - w_{n-1}}{a + u_n - u_{n-1}}\right) - \arctan\left(\frac{w_{n+1} - w_n}{a + u_{n+1} - u_n}\right),$$

where u_n and w_n are the longitudinal and transverse components of the displacement, respectively. The Lagrangian of the system, within a harmonic approximation, has the following form

$$L = \frac{m}{2} \sum_{n=-Z}^Z (\dot{u}_n^2 + \dot{w}_n^2) - \frac{1}{2} \sum_{n=-Z}^Z (\alpha \lambda_n^2 + \beta \kappa_n^2), \quad (1)$$

where α and β are the force constants; the dot denotes derivative with respect to the time t . The number of elemental cells Z in the chain is supposed to be large enough, i.e. $Z \rightarrow \infty$. Equations governing the dynamics of the chain of particles are derived with the help of the Euler-Lagrange principle of variations. For the convenience of asymptotic procedures we introduce a small parameter $\mu \ll 1$, using the following similarity transform: $u_n \rightarrow \mu u_n$, $w_n \rightarrow \mu w_n$. In the linear limit,

as $\mu \rightarrow 0$, equations become linear. Spectral parameters of the linearized set are completely characterized by the following dispersion relations

$$\omega_l(k) = \sqrt{\frac{2}{m}\alpha(1 - \cos ka)}; \quad \omega_b(k) = 2\sqrt{\frac{\beta}{m}\frac{(1 - \cos ka)}{a}}, \quad (2)$$

where $\omega_l(k)$ and $\omega_b(k)$ stand for the natural frequencies of the normal harmonic waves, depending upon the wave number k .

3 Average Hamiltonian. Resonance

Let the small parameter of the problem μ be non-zero. The solution to the linearized set can be adopted to have some useful information on the nonlinear system characterized by the Lagrangian (1), by varying the complex amplitudes of quasi-harmonic waves at the time:

$$\begin{aligned} \mathbf{u}_n(t) &= \int_{-\infty}^{\infty} (A_l(k, \tau_1, \tau_2, \dots) e^{i\phi_l(k,t)} + \text{c.c.}) dk + \sum_{m=1}^{\infty} \mu^m \mathbf{u}_n^{(m)}(t); \\ \mathbf{w}_n(t) &= \int_{-\infty}^{\infty} (A_b(k, \tau_1, \tau_2, \dots) e^{i\phi_b(k,t)} + \text{c.c.}) dk + \sum_{m=1}^{\infty} \mu^m \mathbf{w}_n^{(m)}(t). \end{aligned} \quad (3)$$

Here A_l and A_b are the complex amplitudes (*c.c.* are the corresponding complex conjugates of the preceding terms); $\phi_l(k, t) = \omega_l(k)t + kan$ and $\phi_b(k, t) = \omega_b(k)t + kan$ denote fast-rotating phases of the transverse and longitudinal waves, respectively; $\tau_n \rightarrow \mu^n t$ are the slow temporal time scales; $\mathbf{u}_n^{(m)}(t)$ and $\mathbf{w}_n^{(m)}(t)$ are small nonresonant corrections to the basic solution. The Lagrange function, with the help of anzats (3), being averaged over the fast rotating phases, appears in the form of so-called average Lagrangian $\langle L \rangle$. In turn, the arguments are of this function are proportional to the canonically conjugate variables. If one enters by a standard way the generalized momenta, \mathbf{p}_{A_l} and \mathbf{p}_{A_b} , then the average Lagrangian $\langle L \rangle$ can be rewritten as the average Hamiltonian $\langle H \rangle = \dot{A}_l \mathbf{p}_{A_l} + \dot{A}_l^* \mathbf{p}_{A_l^*} + \dot{A}_b \mathbf{p}_{A_b} + \dot{A}_b^* \mathbf{p}_{A_b^*} - \langle L \rangle$. The advantage of the Hamiltonian description is obvious: at least the one integral of energy is already known *a priori*, $\langle H \rangle = H_0$, where H_0 is a of integration. The average Hamiltonian, as a power series in μ , has a simple structure:

$$\langle H \rangle = \mu^2 \langle H_2 \rangle + \mu^3 \langle H_3 \rangle + \dots$$

The first term $\langle H_2 \rangle$ is identically zero by virtue of the dispersion relations (3). The term $\langle H_3 \rangle$ is a cubic polynomial dependent upon the new generalized coordinates, namely, the complex conjugate amplitudes of longitudinal and transverse waves. This term carries all the information about the dynamic properties of the system within the first-order nonlinear approximation. Let $\langle H_3 \rangle$ be not identically zero. Then the system experiences the first-order *resonance*, due to the nonlinear coupling between triads of modes being in phase, known as the *resonant triplets*.

4 Triple-mode resonant ensembles

For the benefit of nonlinear triple-mode resonant interaction between waves, any dynamical system requires an appropriate type of quadratic nonlinearity in the equations of motion, together with fulfilling the following *phase-matching* conditions

$$\omega_1 = \omega_2 + \omega_3; \quad k_1 = k_2 + k_3. \quad (4)$$

Here ω_n are the natural frequencies and k_n are the corresponding wave numbers of waves, satisfying the dispersion relations (2). The frequencies are numbered following the natural order: $\omega_1 \geq \omega_2 \geq \omega_3$. Based on the analysis of the dispersion and the structure of nonlinearity, one can establish that the triple-mode resonance in a carbyne chain can be of the one single type: each triple can consist of the primary high-frequency longitudinal mode with a pair of transverse low-frequency satellites, being in phase.

Real solutions to the dispersion equation (2), satisfying the phase-matching conditions (4), can be determined graphically. These solutions do exist in the wide permissible range of wave numbers, though the wave number of the longitudinal mode k_1 should not belong to the following "forbidden" interval:

$$k_1 \notin [k^*, 2\pi - k^*], \text{ where } k^* = \arctan \left(\frac{8\sqrt{\alpha\beta}(\alpha a^2 - 4\beta)a}{\alpha^2 a^4 - 24\beta\alpha a^2 + 16\beta^2} \right) / a.$$

5 Evolution equations of a single triad

Let the high-frequency mode of the resonant triad be a longitudinal wave. Then, after substituting the following representation of the solution:

$$\begin{aligned} \mathbf{u}_n(t) &= A_1(\tau) \exp i(\omega_1 t + k_1 a n) + \text{c.c.}; \\ w_n(t) &= A_2(\tau) \exp i(\omega_2 t + k_2 a n) + A_3(\tau) \exp i(\omega_3 t + k_3 a n) + \text{c.c.}, \end{aligned} \quad (5)$$

into the Lagrangian (1), where ω_m and k_m are the spectral parameters of waves entering the resonant triple; $A_m(\tau)$ are the complex amplitudes of quasi-harmonic waves that slowly varying in the time $\tau = \mu t$; *c.c.* denotes the complex conjugate of the preceding terms, the evolution equations describing the evolution of the first-type triad take the following form:

$$2im\omega_j \frac{dA_j}{d\tau} = \frac{\partial H}{\partial A_j^*}; \quad -2im\omega_j \frac{dA_j^*}{d\tau} = \frac{\partial H}{\partial A_j}. \quad (6)$$

Here $H = ic(A_1^* A_2 A_3 - A_1 A_2^* A_3^*)$ is the average potential of the triplet; *c* is the coefficient of the nonlinear coupling.

6 Conservation laws for isolated triads

The evolution equations (6) possess the first integrals. Obviously, one of them, is the average Hamiltonian: $H = \text{constant}$, while the others are known as the Manley-Rowe relations [7]:

$$\begin{aligned} \omega_1 |A_1(\tau)|^2 + \omega_2 |A_2(\tau)|^2 &= c_{1,2}; \\ \omega_2 |A_2(\tau)|^2 - \omega_3 |A_3(\tau)|^2 &= c_{2,3}, \end{aligned} \quad (7)$$

where $c_{1,2}$, $c_{2,3}$ are arbitrary integration constants determined from the initial conditions to the Cauchy problem.

7 The superposition of triads

The average Hamiltonian, related to N resonant triads in a carbyne chain, can be written as it follows

$$H = i \sum_{n=1}^N c_n (A_{3n-2}^* A_{3n-1} A_{3n} - A_{3n-2} A_{3n-1}^* A_{3n}^*),$$

where c_n are the nonlinearity coefficients related to the n -th resonant triplet; A_m ($m = \overline{1, 3N}$) are the complex amplitudes of waves, slowly varying in the time τ . The evolution equations of the triad chain are derived from the Hamiltonian formalism of mechanics:

$$2im\omega_n \frac{dA_n}{d\tau} = \frac{\partial H}{\partial A_n^*}; \quad -2im\omega_n \frac{dA_n^*}{d\tau} = \frac{\partial H}{\partial A_n}. \quad (n = \overline{1, 3N}) \quad (8)$$

These equations can be rewritten in polar coordinates:

$$A_n(\tau) = a_n(\tau) \exp i\varphi_n(\tau) \quad (n = \overline{1, 2N+1}).$$

8 Stationary energy partition in a carbyne chain

The first-principle estimates of the carbyne chain parameters are the following [3]: $E = 32.71$ [TPa]; $a = 32.71 \times 10^{-10}$ [m]; $r = 0.366 \times 10^{-10}$ [m]; $m = 1.994 \times 10^{-26}$ [kg]. These parameters are sufficient for calculating the specific values of the coefficients: $F = \pi r^2 = 0.149 \times 10^{-20}$ [m²]; $J = \pi r^4/4 = 0.017 \times 10^{-40}$ [m⁴]; $\alpha = EF/a = 5.969 \times 10^{-10}$ [TPa \times m]; $\beta = JF/a = 0.222 \times 10^{-30}$ [TPa \times m³]. Here F and J denote the effective cross-section square and moment of inertia, respectively. The flexural rigidity of carbyne at ambient temperatures corresponds to the persistence length about 110 carbon atoms along the chain [3]. The ratio of the de Broglie wavelength to the distance between the nearest neighborhood carbon atoms is about 10^{-1} . This indicates the possibility of studying the wave dynamics of carbyne in the framework of the classical mechanics. Carbyne chain has a small flexural rigidity that satisfies the inequality $\beta/\alpha a^2 \ll 1$. This indicates that the complex cascades of

energy exchange between the modes of oscillations are absent in the system. Within the first-order nonlinear approximation analysis, only the three-wave resonant interactions between high-frequency longitudinal and pairs of low-frequency transverse waves are involved in the formation of steady states. The stationary solution for a single resonant triplet is following

$$\omega_1 \omega_1 \alpha_1^2 = \omega_2 \omega_2 \alpha_2^2 = \omega_3 \omega_3 \alpha_3^2 = \omega_1 \omega_2 \omega_3 \omega_1 \omega_2 \omega_3 / c^2,$$

where ω_i are the nonlinear Stokes corrections to the natural frequencies ω_i . In the first-order approximation, the nonlinear triple wave resonant ensembles represent closed and isolated dynamical objects. Therefore, the principle of linear superposition for any set of triplets should be valid. Therefore, there are infinitely many different patterns of the stationary energy distribution between the individual modes of oscillations of the system, from a formal point of view. Among all these possible stationary distributions, one should choose the single steady state that is implemented in practice. A selection rule provides the Boltzmann theorem on the energy equipartition between degrees of freedom from the statistical mechanics, declaring the proportionality of the average kinetic energy of a particle to the temperature of the system. At the thermal equilibrium, the energy is divided equally between all the modes. In the context of the problem of the stationary energy partition in a carbyne, the following sequence of constructions is evident. At the first step, it is reasonable to assume that nonlinear interactions between the modes are negligible, i.e., the system represents an ideal gas of quasi-particles without collisions. Then the stationary distribution of energy in the chain will be exactly described by the classical Rayleigh–Jeans law, since the total kinetic energy of the system is equal to

$$K = \sum_{n=1}^{3N} K_n = \sum_{n=1}^{3N} \omega_n^2 \alpha_n^2 = 3N k_B T (\alpha^2 \alpha)^{-1},$$

where k_B and T are the Boltzmann constant and the temperature, respectively; $3N$ is the total number of modes entering N different resonant triads. Every oscillatory mode, by virtue of the equipartition theorem, has the energy portion $K_n = \omega_n^2 \alpha_n^2 = k_B T (\alpha^2 \alpha)^{-1}$.

Let us assumed now an essential nonlinearity of the system under consideration. The total kinetic energy is also conserved:

$$K = \sum_{n=1}^{3N} K_n = \text{constant}.$$

The portions of the binding energy are represented by the Hamiltonians of N individual resonant triplets: $H_n = -2c_n \alpha_{3n-2} \alpha_{3n-1} \alpha_{3n}$. Using the Lagrange method, we introduce the following function

$$\Lambda_K = \sum_{n=1}^N H_n + \sum_{n=1}^{3N} \lambda_n (\omega_n^2 \alpha_n^2 - K_n),$$

where λ_n are the Lagrange multipliers, which should be determined together with the amplitudes of oscillations α_n . A minimization of this function leads to the standard

Rayleigh–Jeans law:

$$\alpha_{3n-i} = \sqrt{k_B T (\alpha a^2 \omega_{3n-i}^2)^{-1}} \quad (i = \overline{0, 2}; \quad n = \overline{1, N}).$$

This expression manifests on the proportional amplitude dispersion: the frequency corrections of nonlinear stationary waves, Ω_n , are directly proportional to the natural frequencies of the linear oscillators, ω_n . The coefficients of proportionality is $\sigma_n = c_n \sqrt{k_B T} / (2a \sqrt{\alpha} \omega_{3n-2} \omega_{3n-1} \omega_{3n})$. As one can see, the generalization of the Rayleigh–Jeans law for nonlinear stationary processes is reduced to a frequency shift of linear harmonics, characterized by the ratio: $1 + \mu \sigma_n$, where the small parameter is defined by the maximal amplitude of the given triad: $\mu = \max(\alpha_n)$.

For example, let us consider a resonant triad with the following spectral parameters, almost at the boundary of the "forbidden" zone: $\omega_1 = 0.297$; $\omega_2 = 0.560$; $\omega_3 = 0.261$; $c_1 = 0.298$. Let the temperature be $T = 300$ [K]. The minimum of the functional $\Lambda_K = -0.987 \times 10^{-4}$ is achieved at the point $\varpi_2 = 0.061$. The proportionality coefficient is $\sigma_1 = 0.234$. The maximal amplitude of the stationary process equals to $\mu = \alpha_3 = 0.039$. One can see that the frequency ratio, caused by the proportional amplitude dispersion at room temperature, can be clearly distinguished experimentally: $\mu \sigma_1 = 0.009$, i.e., being about a percents higher, compared to that of the linear theory. At the temperature $T = 600$ [K], this frequency ratio arises almost up to two percents: $\mu \sigma_1 = 0.018$, and so on.

The problem formulation for any arbitrary set of resonant triads in a carbyne chain is reduced to the linear superposition of all waves entering these ensembles, being the closed and isolated dynamical systems, at least within the first-order nonlinear approximation.

9 Conclusion

Central and noncentral interactions between carbon atoms in a carbyne chain are taken into account to investigate the stationary energy partition between waves at ambient temperatures. The study used standard asymptotic methods of nonlinear dynamics, in the framework of classical mechanics, based on most simple mathematical model. The first-order nonlinear approximation analysis revealed the triple-wave resonant ensembles of quasi-harmonic waves. These ensembles are formed due to a quadratic nonlinearity of the system, provided that the triple-mode phase-matching conditions are satisfied. Each resonant triad consists of a single primary high-frequency longitudinal mode and a pair of secondary low-frequency transverse modes of oscillations. It was shown that low-frequency quasi-harmonic longitudinal waves, caused by the central forces, are almost always unstable. These break up into pairs of secondary low-frequency transverse waves, unless the frequency of the primary longitudinal mode does not exceed some critical limit, defined by some "forbidden" zone. In general, the carbyne chain is described as a superposition of resonant triads of different spectral scales. We found that the stationary energy distribution in carbyne chains is described by the standard Rayleigh–Jeans law. This describes an equal energy distribution over the degrees of freedom. Some differences arise due to the effect of the proportional amplitude dispersion, leading to

a temperature-dependent shift of wave frequencies in several percents, that can be clearly distinguished in experiments. These dispersion effect gets higher the theoretical value of the specific heat, and, in turn, can influence upon the thermal conductivity and other phenomenological parameters of the carbyne chain, especially at low temperatures, at which the tools of classical mechanics cannot be applied yet. The present study may be of interest for some applications of nanotechnology, dealing with NEMS or delicate water purification sets.

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