Discrete breathers in polyethylene chain

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The existence of discrete breathers (DBs), or intrinsic localized modes (localized periodic oscillations of transzigzag) is shown. In the localization region periodic contraction-extension of valence C—C bonds occurs which is accompanied by decrease-increase of valence angles. It is shown that the breathers present in thermalized chain and their contribution dependent on temperature has been revealed.

I. INTRODUCTION

Localized excitations in nonlinear systems (solitons, polarons, breathers) became the subject of growing interest during last decades. Discrete breathers, or intrinsic localized modes correspond to shortwave length periodic vibrations which can not be revealed in continuum model of the chain. Intensive study of the breathers has an origin in pioneer work of Sievers and Takeno [1]. Their existence is proved by corresponding theorem [2, 3] and numerous numerical investigations [4]. Nowadays their role in mechanisms of the energy relaxation in molecular systems becomes rather clarified [5, 6, 7].

However all these results relate to simple one-dimensional systems. Meantime it should be waited that similar elementary excitations can exist in more realistic discrete nonlinear models [8]. The necessary conditions for their existence are discreteness of the system leading to boundedness of phonon frequency spectrum and amplitude dependence of eigenfrequencies caused by nonlinearity. These conditions are satisfied for polymeric molecules. For example, anharmonic potential of C—H valence bond in carbon-hydrogen chains leads to existence of high-frequency localized vibrations of such bonds [8]. Naturally, this type of breathers has to be present in polyethylene (PE) chain but corresponding frequencies are very high (~ 3100 cm⁻¹). We will discuss the breathers caused by the backbone vibrations of PE chains which correspond to much more less frequencies because they arise due to coordinated changes of C—C valence bonds and CCC-valence angles.

II. MODEL OF MACROMOLECULAR CHAIN IN PE CRYSTAL

Nonlinear dynamics of planar PE macromolecule has been considered in [9, 10] where a detail consideration of the transzigzag model is presented. This is a reason for only short its description which is given below.

PE crystal consists of parallely packed zigzag chains [PE macromolecules (CH₂)ₙ]. The structure of the crystal is schematically plotted at Fig. 1. Every PE macromolecule in the crystal has a transzigzag conformation. It means that backbone of the chain has a planar zigzag structure with equilibrium length ρ₀ = 1.53 Å of valence bond H₂C—CH₂ and value θ₀ = 113° of valence angle CH₂—CH₂—CH₂. All macromolecules are situated in parallel planes. The crystalline structure is characterized by angle θ₀ and three periods: a = 4.51 Å, b = 7.031 Å, c = 2ρ₀sin(θ₀/2) = 2.552 Å.

![Fig. 1: Schematic representation of the crystalline PE. The central trans-zigzag backbone (curve 0) and the six neighbor chains (curves 1,2,...,6) are shown. The local coordinates for the central chain are presented.](image)

Let us consider the dynamics of PE macromolecule and will take into account its interaction with six neighbor chains which being considered as immobile (approximation of immobile neighbor chains). Because the motion of hydrogen atoms with respect to backbone chain is not significant when studying low energy nonlinear dynamics, we will consider every CH₂-group as a united particle.

Let us introduce the local coordinate system presented at Fig. 1. Then the Hamiltonian of the chain can be written as follows

\[
H = \sum_{n}(\frac{1}{2}M(\dot{u}_n^2 + \dot{v}_n^2 + \dot{w}_n^2) + V(\rho_n) + U(\theta_n) + W(\delta_n) + Z(u_n, v_n, w_n)),
\]  

(1)
where the first term describes the kinetic energy of \( n \)th unit, the second the deformation energy of the \( n \)th valence bond, the third the deformation energy of the \( n \)th valence angle, the fourth the deformation energy of \( n \)th torsional angle, and the last term the energy of interaction of the \( n \)th unit with the six neighboring chains (substrate potential), \( M = 14m_p \) is the mass of the united atom \((m_p \) is the proton mass).

The length of \( n \)th valence bond is

\[
\rho_n = (a_{n,1}^2 + a_{n,2}^2 + a_{n,3}^2)^{1/2},
\]

where \( a_{n,1} = u_n + u_{n+1} - l_x, \ a_{n,2} = v_n + v_{n+1}, \ a_{n,3} = w_{n+1} - w_n + l_z \ [l_x = p_0 \cos(\theta_0/2) \text{ and } l_z = p_0 \sin(\theta_0/2)] \) – transversal and longitudinal step of the zigzag chain. The cosine of the \( n \)-th valence angle is

\[
\cos(\theta_n) = (a_{n-1,1}a_{n,1} + a_{n-1,2}a_{n,2} - a_{n-1,3}a_{n,3}) / \rho_{n-1}\rho_n,
\]

and the cosine of the \( n \)th torsional angle is

\[
\cos(\delta_n) = (-b_{n,1}b_{n+1,1} + b_{n,2}b_{n+1,2} + b_{n,3}b_{n+1,3}) / \beta_n\beta_{n+1},
\]

where

\[
\begin{align*}
  b_{n,1} &= a_{n-1,2}a_{n,3} + a_{n,2}a_{n-1,3}, \\
  b_{n,2} &= a_{n-1,1}a_{n,3} + a_{n,1}a_{n-1,3}, \\
  b_{n,3} &= a_{n-1,2}a_{n,1} - a_{n,2}a_{n-1,1}, \\
  \beta_n &= (b_{n,1}^2 + b_{n,2}^2 + b_{n,3}^2)^{1/2}.
\end{align*}
\]

Potentials of valence bond, valence angle, and torsion angle are accepted in the form

\[
\begin{align*}
  V(\rho_n) &= D_0 \{1 - \exp[-\alpha(\rho - \rho_0)]\}^2, \\
  U(\theta_n) &= \frac{1}{2} \gamma (\cos \theta - \cos \theta_0)^2, \\
  W(\delta_n) &= C_1 + C_2 \cos \delta_n + C_3 \cos 3\delta_n,
\end{align*}
\]

where the parameters \( D_0 = 334.72 \) kJ/mol, \( \alpha = 1.91 \) Å\(^{-1}\), \( \gamma = 130.122 \) kJ/mol, \( C_1 = 8.37 \) kJ/mol, \( C_2 = 1.675 \) kJ/mol, \( C_3 = 6.695 \) kJ/mol. The substrate potential

\[
Z(u, v, w) = \varepsilon_w \sin^2(\pi w/l_z) \left[ u - \frac{1}{2} K_u \{1 + \varepsilon_u \sin^2(\pi w/l_z)\} \right]^2 + \frac{1}{2} K_v \{1 + \varepsilon_v \sin^2(\pi w/l_z)\} v^2,
\]

where the parameters \( \varepsilon_u = 0.0674265 \) kJ/mol, \( \varepsilon_v = 0.0418353 \) kJ/mol, \( \varepsilon_w = 0.1490124 \) kJ/mol, \( K_u = 2.169513 \) kJ/Å\(^2\), \( K_v = 13.683865 \) kJ/Å\(^2\). Detail substantiation of chosen potentials is presented in [10].

### III. LINEAR OSCILLATIONS OF TRANSZIGZAG

Small-amplitude vibrations of isolated transzigzag were considered in [9, 11, 12] and vibrations with account of interaction with immobile surrounding chains – in [10].

Small-amplitude vibrations can be divided on planar (in the zigzag plane) and transversal ones. In turn, the plane motions are divided on low-frequency acoustic and high-frequency optic vibrations. Accordingly, one can separate three dispersion curves corresponding to 1) plane acoustic phonons \( \omega = \omega_a(q) \), 2) plane optic phonons \( \omega = \omega_o(q) \), 3) transversal phonons \( \omega = \omega_t(q) \). These curves with account of interchain interaction are presented at Fig. 2 (a).

![Dispersion curves](image-url)

FIG. 2: Dispersion curves \( \omega = \omega_a(q), \omega = \omega_o(q), \omega = \omega_t(q) \) (curves 1, 2, 3) for trans-zigzag interacting with immobile surrounding chains (a). Density of energy distribution \( p \) on frequencies \( \omega \) for thermal vibrations with temperature \( T = 1 \) K (b), \( T = 100 \) K (c), \( T = 200 \) K (d), and \( T = 300 \) K (e). Gray color corresponds to frequencies region in which the discrete breathers occur.

For isolated chain (substrate potential \( Z(u, v, w) \equiv 0 \)) the acoustic phonons have the frequency spectrum \( 0 \leq \omega_a \leq 228.75 \) cm\(^{-1}\), torsional (transversal) phonons – spectrum \( 0 \leq \omega_t \leq 243.85 \) cm\(^{-1}\), and optic phonons – spectrum \( 383.47 \) cm\(^{-1}\) \( \leq \omega_o \leq 1168.11 \) cm\(^{-1}\). Interaction with surrounding chains leads only to a shift to right of low boundary of acoustic and transversal phonons: \( 19.05 \) cm\(^{-1}\) \( \leq \omega_a \leq 229.54 \) cm\(^{-1}\); \( 52.43 \) cm\(^{-1}\) \( \leq \omega_t \leq 249.43 \) cm\(^{-1}\); \( 838.69 \) cm\(^{-1}\) \( \leq \omega_o \leq 1168.27 \) cm\(^{-1}\).
IV. LOCALIZED NONLINEAR VIBRATIONS OF PE CHAIN

The equations of motion corresponding to Hamiltonian (1) have the form

\[ M \ddot{u}_n = -\frac{\partial H}{\partial u_n}, \quad M \ddot{v}_n = -\frac{\partial H}{\partial v_n}, \quad M \ddot{w}_n = -\frac{\partial H}{\partial w_n}, \quad (2) \]

\[ n = 0, \pm 1, \pm 2, \ldots . \]

Complexity of this system does not allow to find its analytic solution. Therefore we used a numerical procedure.

The finite chain consisting of \( N = 200 \) CH\(_2\) groups was considered. The viscous friction providing adsorption of phonons was introduced on the boundaries of the chain. The system of equations (2) with \( n = 1, 2, \ldots, N \) was integrated numerically with breather-like initial condition. If a discrete breather can exist in the chain it can manifest itself in irradiation of superfluous (non-breather part of initial excitation) phonons.

Numerical modeling has shown that only one type of localized periodic vibrations exists caused by tension-compression of valence C—C bonds with coordinated change of valence angles in the plane of transzigzag — see Fig. 3(b)(c). The vibration occurs in the plane of trans-zigzag with nodes displacements perpendicular to main backbone axis [Fig. 3(a)].

These vibrations are stable excitations, which are characterized by frequency \( \omega \), energy \( E \) and dimensional width

\[ L = 2\left[ \sum_{n=1}^{N} (n - n_c)^2 p_n \right]^{1/2}, \]

where the point \( n_c = \sum_{n} n p_n \) determines the position of the vibrations center and sequence \( p_n = \sum_{n} E_n / E \) — the distribution density of energy along the chain. Essential nonlinearity of these vibrations is manifested in decrease of its frequency with amplitude growth. So, the revealed excitation is actually discrete breather.

Dependence of energy \( E \) and width of the breather \( L \) on its frequency \( \omega \) is presented at Fig. 4. The frequency spectrum of the breather has situated near low boundary of optic phonons. It is a reason why weak intermolecular interaction with surrounding chains do not practically effect on such excitations. If in isolated chain its frequency \( \omega_b = 817 \text{ cm}^{-1} < \omega < \omega_o(0) = 838 \text{ cm}^{-1} \), in the chain surrounding by immobile neighbor chains — \( \omega_b = 820 \text{ cm}^{-1} < \omega < \omega_o(0) = 839 \text{ cm}^{-1} \). When frequency decreases the energy of breather increases monotonically and its width decreases monotonically.

The frequency of breather has to be separated from the frequencies of small amplitude linear vibrations. One could expect also the existence of low-frequencies breathers with frequencies near upper boundary of transversal phonons \( \omega > \max \omega_i(q) \) and high-frequency breathers with frequencies near upper boundary of optical phonons \( \omega > \omega_o(\pi) \). But numerical analysis has shown that such localized excitations are absent.

V. THERMAL VIBRATIONS OF TRANS-ZIGZAG AS ORIGIN OF DISCRETE BREATHERS

Let us consider the thermal vibrations of trans-zigzag. With this goal we analyze the finite chain consisting of \( N \) segments. Their \( N_0 \) segments near boundary (from both sides) are situated into heat bath with temperature \( T \). The dynamics of the system is described by the systems of Langevin equations

\[ M \ddot{u}_n = -\frac{\partial H}{\partial u_n} + \xi_n - \Gamma_n M \dot{u}_n, \]

\[ M \ddot{v}_n = -\frac{\partial H}{\partial v_n} + \eta_n - \Gamma_n M \dot{v}_n, \]

\[ M \ddot{w}_n = -\frac{\partial H}{\partial w_n} + \zeta_n - \Gamma_n M \dot{w}_n, \]

\[ n = 1, 2, \ldots, N, \]

where the Hamiltonian of the system \( H \) is given by Eq. (1), \( \xi_n, \eta_n, \) and \( \zeta_n \) are random normally distributed forces describing the interaction of \( n \)th molecule with a thermal bath, the
coefficient of friction $\Gamma_n = 0$ for $N_0 < n \leq N - N_0$ and $\Gamma_n = \Gamma$ for $n \leq N_0$ and $N - N_0 < n \leq N$. Coefficient of friction $\Gamma = 1/t_r$, where $t_r$ - the relaxation time of the velocity of the molecule. The random forces $\xi_n$, $\eta_n$, and $\zeta_n$ have the correlation functions

$$
\langle \xi_n(t_1) \xi_m(t_2) \rangle = \langle \eta_n(t_1) \eta_m(t_2) \rangle = \langle \zeta_n(t_1) \zeta_m(t_2) \rangle = 2M\Gamma k_B T \delta_{nm} \delta(t_1 - t_2), \\
\langle \xi_n(t_1) \eta_m(t_2) \rangle = \langle \xi_n(t_1) \zeta_m(t_2) \rangle = \langle \eta_n(t_1) \zeta_m(t_2) \rangle = 0,
$$

where $k_B$ is Boltzmann’s constant and $T$ is the temperature of the heat bath.

The system (3) was integrated numerically by the standard forth-order Runge-Kutta method with a constant step of integration $\Delta t$. Numerically, the delta function was represented as $\delta(t) = 0$ for $|t| > \Delta t/2$ and $\delta(t) = 1/\Delta t$ for $|t| \leq \Delta t/2$, i.e. the step of numerical integration corresponded to the correlation time of the random force. In order to use the Langevin equation, it is necessary that $\Delta t \ll t_r$. Therefore we chose $\Delta t = 0.001$ ps and the relaxation time $t_r = 0.1$ ps.

Let us consider a frequency distribution of kinetic energy of thermal vibrations. For this goal the system (3) was integrated numerically for $N = 500$, $N_0 = N/2$. While choosing the initial conditions as corresponding to ground state of the chain the system was integrated during $t = 10t_r$, to bring it in the thermal equilibrium. After that we calculated the density of molecules kinetic energy distribution on frequencies $p(\omega)$. To increase an accuracy, the density of distribution was calculated using 1000 independent realizations of the chain thermalization. The profile of the density of distribution for different values of temperature is presented at Fig. 2 (it is accepted that $\int p(\omega)d\omega = 3$).

For temperature $T = 1$ K the density of distribution coincides practically with corresponding density for linearized system, so anharmonicity is here not essential. All vibrations are linear and only phonons are thermalized. With further increasing of temperature the amplitude of thermal vibrations also increases so their anharmonism is manifested. For $T = 100$ K we see a shift of density behind the low boundary of the spectrum of optic phonons which becomes more pronounced with further increase of the temperature. High frequency vibrations in this region can be identified as breathers because they arise in the frequency region $[\omega_b, \omega_b(0)]$, corresponding to this type of excitations. The part of energy corresponding to breathers may be found as

$$
p_b = \int_{\omega_b}^{\omega_b(0)} p(\omega)d\omega.
$$

The contribution of the breathers in thermal energy increases with growth of temperature (for $T = 1$ K it is $p_b = 0.002$, for $T = 100$ K — $p_b = 0.106$), has a maximal value $p_b = 0.115$ for $T = 200$ K and then decreases (for $T = 300$ K the breathers contribution corresponds to $p = 0.083$).

Let us isolate the breathers from thermal vibrations. With this goal we consider the chain consisting $N = 500$ segments with boundary cites ($N_0 = 50$) embedded to the heat bath with temperature $T$. After thermalization, we put the temperature of thermal bath $T = 0$ and consider the irradiation of heat energy from internal region ($N_0 < n < N - N_0$). The relaxation process for $T = 200$ K is shown at Fig. 5. We see a formation of several mobile localized excitations. Their detail analysis leads to conclusion that they are discrete breathers with frequencies $\omega \sim \omega_b$. So, one can observe the presence of breathers in thermal vibrations.

Let us consider the interaction of discrete breather with thermal phonons. The stationary discrete breather with frequency $\omega = 820.5$ cm$^{-1}$ was situated in the center of finite chain ($N = 200$), their edges ($N_0 = 10$) being situated in thermal bath ($T = 10$ K). As we can see from Fig. 6 the breaking of breather is observed just as the center of the chain is thermalized (the energy loss is 50% for 20 ps).

Probability of thermally activated formation of discrete breathers in the chain grows with increasing of the temperature. Therefore their concentration has to increase when temperature grows. However in a thermalized chain the breather has a finite time of life, decreasing with growth of the temperature. It is reason for non-monotones dependence of the concentration of breathers $p_b$ upon temperature $T$ — it increases when $T \leq 200$ K and decreases for $T > 200$ K with maximal magnitude for $T = 200$ K. Numerical study shows that the breathers may be better separated from thermal vibrations namely when $T = 200$ K.

FIG. 4: Dependence of energy $E$ (a), width $L$ (b) of the breather upon frequency $\omega$ in isolated chain (curves 1, 3) and in the chain with substrate potential (curves 2, 4).
FIG. 5: Formation of discrete breathers from thermal vibrations of zigzag chain \((N = 500, \; T = 200 \text{ K})\). The absorbing ends are considered \((N_0 = 50)\). Temporal dependence of energy distribution \(E_n\) in the chain is presented.

One can see from Fig. 2 that revealed breathers is a unique type of stable localized periodic excitations in thermalized chain for given parameters of the crystal. Besides the breathers only vibrations with frequencies possessing to spectrum of linear oscillations can be thermalized. It confirms the conclusions with respect to existence of only one stable type of discrete breathers corresponding to localized oscillations of valence C—C bonds. The breathers present in thermalized chain even for sufficiently small temperatures.

VI. CONCLUSION

Stable localized nonlinear vibrations which are discrete breathers can exist in polymer crystal. In PE macromolecule they are planar vibration of transzigzag with periodic deformation of valence bonds C—C and valence angles CCC. The breathers present in thermalized chain and their contribution in heat capacity may be essential.

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