Discrete breathers in realistic models: hydrocarbon structures

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Abstract

Discrete breathers (DBs), or intrinsic localized modes, are time-periodic spatially localized solutions that exist generically in nonlinear discrete models and persist as long-lived robust solutions when they are not resonant with linear excitations. Without using the powerful but rather technical self-consistent methods of calculation already developed and applied to DBs in relatively simple models, we study DBs with tight-binding molecular dynamics simulations using a realistic model for carbon–hydrogen systems. We focus here on the carbon–hydrogen stretch vibrations, whose frequencies are well separated from the rest of the vibrational modes. We show that in the anharmonic region of the interaction potential these spatially localized solutions persist for time scales which are orders of magnitude longer than the period of the atomic vibrations and with frequencies that are different from the normal-mode frequencies. The conditions under which these DB solutions are created, the implications on energy relaxation, and experimental evidence of their existence are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The concept of self-localization (or self-trapping) of excitations due to the anharmonicity in nonlinear models has been studied extensively over the last few decades (polarons, solitons, breathers). A relatively recent development is the discovery of the, so-called, discrete breathers (DBs) or intrinsic localized modes (ILMs) [1]. These are spatially localized and time-periodic solutions of discrete nonlinear models. Their existence, which is proven by rigorous theorems [2,3] and a large amount of numerical results (see Ref. [4] for a review), is not restricted to special or integrable models. On the contrary, they can be found, in principle, in any discrete, nonlinear system and in any dimension. Discreteness is essential because the phonon spectrum is bounded, and anharmonicity because the amplitude of the vibrations is frequency-dependent. Thus, DBs can persist as exact, linearly stable solutions with frequencies that are non-resonant with the linearized spectrum in discrete nonlinear systems. Experimental observations of DBs are beginning to accumulate recently in a variety of contexts such as coupled nonlinear optical wave guides [5,6], arrays of coupled Josephson junctions...
[7,8], highly nonlinear materials [9], magnetic systems [10] and possibly in myoglobin [11].

Most of the work around DBs up to now involves their general properties and is based on relatively simple anharmonic models. Moreover, it is mainly focused on periodic lattices. We have shown by developing new self-consistent numerical methods that in disordered systems localized DBs exist even with frequencies that are inside the linear spectrum and that belong to Cantor sets with finite measure [12,13]. The gaps where localized DBs do not exist, are due to resonances with the Anderson modes. The width of these resonance gaps decreases when the distance between the DBs and the Anderson mode’s spatial location increases. Inside the gaps, localized DB solutions delocalize becoming multi-DBs and restoring the ability to propagate energy [14]. In fact, a targeted energy transfer between DBs can be achieved under certain conditions [15], which are illustrated in a clear but non-trivial manner in the nonlinear dimer [16]. It is clear by now that the concept of DBs is quite universal and that they should play an important role in nonlinear physical systems.

The purpose of this paper is to show the importance of DBs for a universal understanding of localized time-periodic excitations in discrete nonlinear systems, independent of model or structural complexity. Understanding DBs in realistic models is crucial for a variety of phenomena in condensed matter physics, chemistry, biological physics and other disciplines. Systems containing carbon and hydrogen (C–H) are important in this aspect. In this work, we use a realistic tight-binding molecular dynamics (TBMD) scheme to show that DBs exist in systems with carbon and hydrogen. Here we restrict our study to the C–H stretch vibrations whose frequencies are higher and well separated from the rest of the vibrational spectrum. This reduces the possibility of resonances that destroy DBs. We find that, in general, small amplitude initially localized C–H stretch excitations around the equilibrium result to equipartition of energy among normal modes. On the contrary, large amplitude excitations that are clearly anharmonic, remain localized for time scales that are orders of magnitude larger than the atomic vibration periods. We show that these localized excitations are time-periodic with frequencies close to but different from the normal mode frequencies, i.e., they are DBs.

In the next section, we briefly review the TBMD simulation scheme. We then present molecular dynamics (MD) results on hydrocarbon molecules (where the concept of local modes is very old for highly excited vibrational states), for long-lived, spatially localized and time-periodic vibrations (“mini” DBs). Then, we extend our presentation to bigger C–H clusters. In the last section, we explain how our results are totally consistent with classical DBs and how a quantum theory of DBs will affect them. We also discuss the conditions of low temperature and low density for these intra-molecular processes.

2. Simulations and results

In order to study the dynamics of C–H systems one needs to have a reliable way of calculating the interatomic forces. Classical MD methods [17] can handle a large number of atoms for relatively long simulation times but fail to describe electronic properties. First-principles MD [18] describe accurately the interatomic interactions but are limited to small systems and short times. TBMD is a semi-empirical scheme that preserves the main quantum mechanical features of the systems while allowing for computer simulations of relatively large systems and long times. The details on TBMD have been described elsewhere [19]. Here we briefly give the main points of the method. In TBMD the system is described by the Hamiltonian

\[ H = \sum_i \frac{p_i^2}{2m_i} + \sum_n \langle \psi_n | H_{\text{TB}} | \psi_n \rangle + E_{\text{rep}}. \]  

The first term on the right-hand side of Eq. (1) is the kinetic energy, \( E_k \), of the atoms \( i = 1, \ldots, N \) with momentum \( p_i \) and mass \( m_i \). The second term is the electronic band structure energy, \( E_{\text{bs}} \), i.e., the sum of the eigenvalues over all occupied electronic states. The electronic eigenvalues are obtained by diagonalizing \( H_{\text{TB}} \) at each time-step of the MD simulation. The matrix elements of \( H_{\text{TB}} \) are adjustable parameters that are determined by fitting to ab initio results. The off-diagonal matrix elements are
two-center hopping parameters, scaled with the interatomic separation with a specific functional form which is nonlinear. The last term, \( E_{\text{rep}} \), includes all the repulsive energies and is also described by short-ranged nonlinear functions of the interatomic distance. For the carbon–carbon interactions the model developed by Xu et al. [20] is used. In order to guarantee transferability of the model, the parameters were obtained by fitting simultaneously to first-principles local density approximation (LDA) results for the energy-vs.-volume curves of infinite linear carbon chain, graphite, diamond, simple cubic, and face-centered cubic structure. This model reproduces correctly properties that do not enter explicitly in the fitting process for the different bonding configurations of carbon. When used in the TBMD scheme, it has been proved to be very successful in describing the structural, vibrational and electronic properties of carbon systems [19] that range from carbon microclusters and fullerenes to amorphous and liquid carbon. Even purely anharmonic effects, such as the temperature dependent phonon frequency shifts and line widths of diamond and graphite are very well described with this model [21], in excellent agreement with experiments. The parameters for the C–H interactions are obtained by fitting to the electronic structure, binding energy and vibrational frequencies of methane (CH\(_4\)). More specifically, the hopping parameters between the s orbital of H and the s and p of C as a function of the interatomic separation, \( r_{\text{CH}} \), were fitted to the ab initio electronic levels and bending modes of the CH\(_4\) molecule for different \( r_{\text{CH}} \). The on-site energy for hydrogen, \( E_{\text{H}} \), was determined by the ab initio results of Mulliken charge population at each atom of CH\(_4\). The repulsive interaction between C and H atoms is fitted to the LDA result for the binding energy of CH\(_4\). In Fig. 1 we present the binding energy of a pair of C–H atoms in CH\(_4\), \( E_{\text{bind}} = E_{\text{bs}} + E_{\text{rep}} \), as a function of \( r_{\text{CH}} \), in our model. In the magnification of Fig. 1(b), the anharmonicity of the interaction is evident (the dotted line showing a harmonic fit close to the equilibrium).

The above model for C–H interactions gives very good results for hydrocarbon molecules since it is based on methane. The model reproduces correctly the structures, binding energies and vibrations of CH\(_4\), C\(_2\)H\(_4\) and C\(_2\)H\(_8\) [22], as well as the properties of longer hydrocarbon chains and of interstitial hydrogen in diamond. From our tests of several properties on a number of hydrocarbon molecules we conclude that our TB model describes successfully the C–H bonding in the molecular environment, although originally made for studying solids such as a-C:H [23].

The time step used in the MD simulations was \( 0.70565 \times 10^{-16} \) s. Our starting configurations are low-temperature relaxed structures that were obtained by cooling from higher temperatures. Our

![Fig. 1. The binding energy \( E_{\text{bind}} \) of a C–H pair in CH\(_4\) as a function of the interatomic separation \( r_{\text{CH}} \) (a). Same in (b) close to the equilibrium distance \( r_{\text{CH,0}} = 1.104 \) Å. The dotted line is a harmonic fit close to \( r_{\text{CH,0}} \).](image-url)
aim is to study the time evolution of an initially localized amount of energy in C–H systems. For that purpose, we excite a H atom and follow the relaxation process, without any temperature control, thus simulating the intra-molecular processes and ignoring inter-molecular interactions in this first approach. This is important for the creation and stability of breathers and corresponds to a low-density regime, where thermal collisions with other molecules can be ignored for our timescales. For comparison purposes, we thermalized the relaxed configurations at the same energy using temperature control, thus simulating thermal collisions. In all examples we present, we used both the former (a H atom displaced from equilibrium along the C–H stretch direction) and the latter (thermalized) initial conditions. We will not present results from any other initial configurations, such as pure bending displacements or “mixed” displacements (with components along several modes of vibration) since we found that it is essentially the C–H stretch components that result in energy localization. This is due to the fact that the rest of the modes are much closer together and DBs that could localize energy resonate with these phonons and quickly decay, as opposed to the C–H stretch which are well separated in the spectrum. The choice of a relatively small time step guarantees the conservation of energy during this MD relaxation. We monitor the positions and velocities of all atoms and we obtain the vibrational spectrum by Fourier transforming the velocities. We have analyzed in detail every atom and every spatial component. Here we try to summarize our findings and present some examples in a condensed manner.

Localized vibrations have already been observed in hydrocarbon chains and interpreted as DBs with a lifetime of a few ps [24]. The initial conditions were localized deformations of the C chain. In Fig. 2 we present such a chain, the \( \text{C}_{22}\text{H}_{24} \) molecule, at equilibrium, with all atoms labeled from 1 to 46. However, in our study, we initially excite a H atom. When we excite, for example, the H atom labeled by 28 in the \( \gamma \)-direction, i.e., the C–H stretching vibration, by \( \Delta y = 0.01 \, \text{Å} \), which corresponds to an energy increase \( \Delta E = 0.0016 \, \text{eV} \), the initially localized energy is spreading more or less uniformly along the chain. For this small initial displacement, the harmonic approximation is valid and normal vibrational modes are excited with spatial equipartition of energy. However, this is not the case with an initial displacement of \( \Delta y = 0.1 \, \text{Å} \) for H atom 28 (i.e., well within the anharmonic part of the potential, Fig. 1). In Fig. 3, the kinetic energy of the initially excited atom 28 and its nearest-neighbors as well as a remote H atom is plotted as a function of time during the first 7 ps approximately. The energy \( \Delta E = 0.1385 \, \text{eV} \) remains mainly localized at the site of the initial excitation. In the spectrum now there is a main peak at 3072 cm\(^{-1}\) that appears in the region of the C–H stretch (which was absent in the weak perturbation of \( \Delta y = 0.01 \, \text{Å} \)) and the (much weaker now) peak at 3092 cm\(^{-1}\), which corresponds to a normal mode. The localized periodic vibration with a frequency different from that of the phonon mode is evidence for the presence of DB. We hope to illustrate here that the energy localization due to the anharmonicity of the interaction potential is a rather general feature of C–H vibrations, due to the formation of DBs. We will present the case of benzene in detail, but a similar analysis applies to a large number of hydrocarbons.

For benzene (\( \text{C}_6\text{H}_6 \)), we first thermalized and then obtained the room temperature vibrational spectrum, in overall agreement with experiments. We started from the zero temperature equilibrium configuration (Fig. 4) and excited a hydrogen atom in several ways. In Fig. 5 we plot the kinetic energy \( E_{ki} \), for \( i = 7, \ldots, 12 \) of the hydrogen atoms as
Fig. 3. The kinetic energy of some H atoms, $E_{kh}$, in units of eV, vs. time during the first 7 ps of the relaxation. The initial condition is with the H-atom 28 of Fig. 2 displaced by 0.1 Å along the C–H stretch direction.

Fig. 4. The equilibrium configuration of C₆H₆. The C–H distance is $r_{CH0} = 1.100$ Å and the C–C distance is $r_{CC0} = 1.396$ Å.

A function of time for the first $10^5$ time steps of the MD simulation. The hydrogen atom labeled 7 in Fig. 4 is initially displaced in the x-direction (pure stretching) by 0.01 Å, i.e., approximately 1% of the equilibrium C–H distance. This corresponds to an energy increase of $\Delta E = 0.0016$ eV with respect to the equilibrium. The energy initially at atom 7 is rapidly distributed among all atoms of the molecule. The frequencies of the vibrational spectrum for $\Delta x = 0.01$ Å are the normal modes allowed by symmetry. When we thermalize with the same energy $\Delta E = 0.0016$ eV we find the same frequencies (with different relative intensities), plus others (that correspond to in-plane bending and out-of-plane modes). In Fig. 6(a) we present the normalized spectrum obtained during the time interval 7–42 ps of the relaxation after the initial $\Delta x = 0.01$ Å so that the spectral resolution is approximately 1 cm⁻¹. The C–H stretch appear with a large intensity comparing to the rest of the modes due to the initial C–H stretch excitation. They are found at 3097, 3101, 3106 (see zooming in the 3050–3150 cm⁻¹ region in Fig. 6(a)), with one of them doubly degenerate. The much weaker lines are at
Fig. 5. The kinetic energy, $E_1$ (eV) of the H-atoms of benzene (Fig. 4) vs. time during the first 7 ps of the relaxation. The initial condition is with the H-atom 7 displaced by 0.01 Å along the $x$-direction.

Fig. 6. The vibrational spectrum when a H atom is initially displaced by $\Delta x = 0.01$ Å in (a), and after thermalization with the same energy $\Delta E = 0.0016$ eV in (b).

562, 960, 1015, 1508 and 1677 cm$^{-1}$. In Fig. 6(b) we plot the normalized spectrum after thermalization. The intensities of the in-plane and out-of-plane bending modes which appear are much bigger than in (a), since now the molecule is randomly excited. The main peaks are at 366, 562, 960, 996, 1015, 1677, 3097, 3105 cm$^{-1}$. In both cases there is energy equipartition in the real space, i.e., among
Fig. 7. The kinetic energy of H atoms, $E_{ki} (\text{eV})$ vs. time during the first 7 ps of the relaxation. The initial condition is with the H-atom 7 of Fig. 4 displaced by 0.1 Å along the $x$-direction.

all atoms of the $C_6H_6$. Even when one H atom is excited (in the C–H stretch direction in our example), the vibration quickly spreads to all atoms, just as with thermalization. From Figs. 6(a) and (b) it is apparent that the initial condition is important for the energy partition among the normal modes. When the C–H stretch is initially excited, the intensity of the relevant modes is very high, as opposed to the case of thermalization.

Fig. 7 is the same as Fig. 5, except for the initial displacement in the $x$-direction which is now 0.1 Å, i.e., of the order of 10% from the equilibrium, well within the anharmonic part of the C–H interaction (Fig. 1). The corresponding excitation energy is now $\Delta E = 0.1391 \text{ eV}$ and as is obvious from Fig. 7 it remains mostly localized at the site of the initial displacement from the equilibrium. A small part goes to the rest of the atoms but the DB which is now created remains stable and prevents energy propagation (at least for simulation times up to ns).

The situation is very different when we thermalized at the same energy $\Delta E = 0.1391 \text{ eV}$. A closer look shows that the period of the localized C–H stretch vibration is different (smaller) from the normal mode C–H stretch, which is an additional evidence that it is a new DB solution. By Fourier transforming the velocities of all atoms we see that the motion of atoms 1 and 7 in the $x$-direction is almost entirely dominated by the DB. The rest of the atoms are clearly vibrating with normal mode components as well. Here we present the total normalized intensity in Fig. 8. We used $5 \times 10^5$ time steps (time interval 35–70 ps for (a) and 35 ps of relaxation after thermalization for (b)). In Fig. 8(a) the DB peak dominates at $v_b = 3080 \text{ cm}^{-1}$. In the bottom magnification around the C–H stretch region we see clearly the peaks that correspond to the normal C–H stretch at 3097 and 3104 cm$^{-1}$. The top inset in (a) is the spectrum on a smaller intensity scale. One can see the rest of the modes.
that are weakly excited in comparison with the DB mode. They are at 562, 960, 1015, 1508, 1677 cm\(^{-1}\), just like in Fig. 6(a). In Fig. 8(b) we present the vibrational spectrum of a thermally excited molecule at the same energy \(\Delta E = 0.1391\) eV. There is no energy localization and the excited modes have comparable intensities. As was the case of the thermalized initial condition at the smaller energy \(\Delta E = 0.0016\) eV, the C–H stretch modes are weak in comparison with the bending modes. The peaks are at 365, 560, 995, 1011, 1114, 1356, 1363, 1673 cm\(^{-1}\), i.e., there is a small frequency softening with respect to Fig. 6(b), which is expected since temperature increased (\(\Delta E = 0.0016\) eV = 19 K while \(\Delta E = 0.1391\) eV = 1614 K).

In Fig. 9(a) we plot the displacement \(\Delta x\) in the x-direction from the equilibrium for the H-atoms of benzene when atom 7 is initially displaced by \(\Delta x = 0.174\) Å, which corresponds to \(\Delta E \approx 0.38\) eV, i.e., the first quantum excited state. The vibration is localized at atom 7 in the C–H stretch direction. In Fig. 9(b) we show the corresponding spectrum (obtained during the time interval 7–35 ps), with the DB at frequency 3068 cm\(^{-1}\). We have to point...
out that the same pattern is repeated in higher energy excitations. As we explain in the next section, the specific example we presented in Figs. 7 and 8 is physically unrealistic due to the zero-point motion, but our results are similar for higher excitations where we approach the classical limit.

In Fig. 10 we show the equilibrium configuration of a cluster consisting of 26 C atoms in a diamond crystal structure and 30 H atoms saturating the “dangling” bonds on the “surfaces”. In Fig. 11 we plot the kinetic energy of some H atoms as a function of time during the first 7 ps of the relaxation. The initial condition is the relaxed structure of Fig. 10 with the H atom 27 displaced in the z-direction by approximately 0.17 Å (pure C–H stretch). The energy (which is higher than the first excited quantum state) stays very localized on this atom (notice the different scales of energy in Fig. 11). In Fig. 13(a) we show the corresponding spectrum (obtained during the first 7 ps), where the DB peak is pronounced at 3030 cm$^{-1}$. In the magnification one can see a lot of other modes very weakly excited in the region 500–1500 cm$^{-1}$.

We will deal with C–C stretch DBs in the future in detail. Here we just present an example to show that localized C–C vibrations do persist like C–H vibrations, but the situation is more complicated due to the excitation of several modes. If one does not start with an exact DB solution, the general picture is like the one shown in Fig. 12. C-atom 14 is initially displaced by 0.1 Å in the C–C stretch direction w.r.t. C-atom 1, and the time evolution of the kinetic energy of a few C atoms is plotted for the first 7 ps. It is clear that the C–C vibration remains localized at the atoms 1 and 14 but the overall behavior of the system is more complex. In Fig. 13(b) we see that a lot of frequencies close to each other appear. Exact DB solutions in this case would involve specific excitations of neighboring C atoms which are not as simple as C–H stretch vibrations.

3. Discussion and concluding remarks

The results presented in the previous section serve to illustrate, without any ambiguity, that classical localized vibrations due to anharmonicity persist with very large lifetimes in realistic models. They have frequencies that are different from and non-resonant with the normal mode frequencies, i.e., they are DBs. We should point out, though, that just like any other molecular dynamics scheme, TBMD treats vibrations classically. TBMD goes further than conventional interatomic potentials used in the study of DBs, since the electronic hamiltonian is diagonalized at every time-step and the specific models we use are fitted to first principles results. However, we have to be careful in the interpretation of the simulations, since classical vibrations could be a severe approximation, especially in the case of H-atoms in the low energy vibrational states.

Within our approach (classical vibrations and quantum electrons), our results are not at all surprising from the DBs point of view. The electrons, which are in their ground state, follow adiabatically the atoms. We start with a localized vibrational excitation which does not correspond to an exact DB solution. The system relaxes to a DB with a small part of energy spread to normal modes. In the case of $C_6H_6$, an initial C–H stretch displacement of 0.1 Å corresponds to a very weak coupling between two nearest-neighbor H-atoms ($7 \times 10^{-5}$ eV with frozen phonons). Thus, we are close to the anticontinuous (uncoupled) limit for the C–H oscillators, where DBs are certain to exist. This limit is the starting point for the proof of...
existence of DBs in Klein–Gordon chains [2]. When the anharmonic oscillators are uncoupled, they become integrable and one can always find a time-periodic solution. The implicit function theorem guarantees that this solution persists for a non-zero coupling. In general, the main idea behind most of existence proofs of DBs is the continuation of the solution from an appropriate “anticontinuous” limit. In diatomic Fermi–Pasta–Ulam chains, the anticontinuous limit is at zero coupling between the diatomic oscillators and a zero-mass ratio of the two types of atoms. The continuation is guaranteed for finite, but small, coupling and mass ratio [25]. In the case of C–H stretch vibrations, we are close to this limit (weak coupling and mass ratio of about 1/12). If one adds to this the large gap between C–H stretch frequencies and the rest of the linear modes (non-resonance condition satisfied), classically speaking, the conditions are very favorable for DBs. The same is true for the rest of the geometries we presented. We did not find DBs in CH₄. In this case, H-atoms are coupled rather strongly through the one C atom and localized C–H vibrations spread rapidly (this cannot exclude however the existence of DBs in CH₄ for different amplitudes of oscillation). One important remark is that our TB models are essentially two-body potentials, so that they might easily sustain localized vibrations. We could add to our model some environment dependence or some extra coupling between stretching and bending modes, like classical three-body potentials do, but DBs should persist in such models as well (to a smaller degree).

We chose to present benzene in detail, since it has been studied extensively from the early days of modern physics and chemistry. In fact, the concept of local modes emerged in 1920s from the study of
Fig. 12. Kinetic energy of some C atoms, $E_{ij}$ (eV) vs. time during the first 7 ps of the relaxation. The initial condition is with the C atom 14 of Fig. 10 displaced by 0.1 Å along the z-direction.

Fig. 13. The vibrational spectrum that corresponds to Fig. 11 in (a) and to Fig. 12 in (b).

Small polyatomic molecules [26,27]. The spectroscopic features of “highly” excited vibrational states are explained on the basis of local modes. This has been already appreciated by nonlinear physicists (for a good discussion on the history of local modes, see [28]) and chemists [29]. The “self-trapping” or Discrete Nonlinear Schrödinger Equation (DNLS) has been used to interpret them in a largely
empirical approach where parameters are fitted directly to spectroscopic data of overtones [28]. In the transferable TB model we use, parameters are fitted only to the C bonding configurations and to methane. In general, when local modes are used, they are not treated within the more general DB context. We also have studied cases of highly excited vibrational states in benzene, and we found DBs, many of them decaying after a few ps. Experiments give similar lifetimes to these local modes but before comparing with experiments we have to analyze the decay mechanisms of our breathers. In simple models, it is found that this is a non-trivial process [30]. Phonons can interact with internal modes of DBs, eventually destroying them, but in some cases they pump energy to them. When phonons are present, we cannot rigorously speak of DBs, and this is the case for initial conditions that do not correspond to an exact DB solution. We will present calculations based on adapting our self-consistent methods for simple models [12-14] to this TB model, where exact non-resonant DBs can be identified. We have to point out that these methods differ from the traditional search for periodic orbits in continuation of minima of potential energy surfaces [31]. We have shown that most DB solutions are not in continuation of linear modes [12].

The specific example of DB in benzene we present in Figs. 7 and 8(a) has an additional pedagogical interest since it demonstrates classical DBs in an “ideal” situation, but at the same time it forces us to confront with the limitations of classical vibrations. Quantum mechanically, it corresponds to an excitation lower in energy than the first excited vibrational state. In our treatment, we do not take into account the zero-point motion. If one tries to relate to quantum mechanics, it should be viewed as a combination of the fundamental and excited states. The fact that DBs are observed in such small energies demonstrates that using the harmonic normal modes obtained from the second-order expansion of the energy around its classical equilibrium state is not correct. Using a semiclassical quantization of classical DBs would also be incorrect because the zero-point motion in the quantum ground-state energy of the molecule would involve displacements larger than the classical DBs amplitudes. A correct approach would be to use a Hartree type of method in this case, in order to find the proper fundamental state. The proof of existence for classical DBs has been recently extended to quantum DBs [32]. At the anticontinuous limit, there is a zero width degenerate band of quantum DBs for each integer n corresponding to the quantum number of the excited state of the uncoupled oscillator. Each DB band can be globally continued from this limit up to a finite perturbation which depends on n. Since our system is very close to the anticontinuous limit, even the first excited DB state, n = 1, of the C–H stretching should not be correctly described as a harmonic normal mode. Since DBs are very localized, a better approach would be to use a quantum equivalent to the classical action-angle representation of the uncoupled anharmonic oscillators. With the creation operator $a^+_n$ defined as $a^+_n |n\rangle = \sqrt{n+1} |n+1\rangle$ and $a_n$, its conjugate (like for the harmonic oscillator), the hamiltonian of the single oscillator is $H_i = E(a^+_n a_n)$. Hamiltonians $H_i$ are weakly coupled. In general, there is no reason that the global Hamiltonian should conserve the number of bosons, $\sum_i a^+_i a_i$. However, in the spirit of the approximation of Ref. [16] for two weakly coupled classical anharmonic oscillators or DBs, the total action is conserved at weak coupling, which corresponds to conservation of $\sum_i a^+_i a_i$ in the quantum case. We thus recover, after expansion at the lowest significant orders, expressions of the type $E(n) = \omega_0 n \pm bn^2 + \cdots$ already considered within DNLS [28], but more general and with clear assumptions. This work is underway.

We only presented periodic structures here in order to show the effects of anharmonicity pure and simple, but DBs can equally be found in amorphous anharmonic systems. The phenomenon is independent of geometry, as long as DBs are non-resonant with phonons. They will eventually decay through coupling with the electromagnetic field (we can add the interaction of dipole moment with the field to our simulations) but in almost macroscopic time w.r.t. the atomic vibrations.

The DB problem for C–C vibrations has been treated in Ref. [24] for linear hydrocarbon molecules, but the results are not conclusive. The DB frequency lies in the band of linear oscillations and there is a rapid decay. In future publications we will
also present DBs in pure C systems. The task of finding DBs in this case is more delicate due to many resonances with linear phonons and geometrical considerations.

Our purpose in this paper was to illustrate the concept of DBs as long-lived localized vibrations in a realistic model through real-time simulations, without going through the technical details of DB theory. We showed how DBs are created with a local excitation and how a phenomenological thermostat suppresses them. This is the reason why they pass unnoticed in MD simulations, when one carefully but, very often, artificially “thermalizes” the system. DBs can appear in MD simulations out of thermodynamic equilibrium even without a local initial excitation. The case of excited polarons in lattices is an example, where a characteristic “anti-thermodynamic” behavior was observed [33]. In fact, we can now identify these excitations as “polarobreathers”.

The experimental evidence of local modes (mini DBs) in isolated hydrocarbon molecules is abundant. In order to observe them one needs low densities and temperatures, conditions that exist in the interstellar medium. Independent of the detailed structure of interstellar dust (molecular, amorphous or crystalline structures), the consensus is that it is mainly composed of C–H systems. Then, the so-called “unidentified infrared bands” could be explained in terms of excitations that include DBs [34]. One of the puzzles is the high temperature of the C–H stretch in space regions that are away from a radiative source. DBs, independent of the heating mechanism, could give an explanation to the observations.

Even though DB theory and methods originate from non-linear lattice dynamics, we believe that they provide us with a unified approach of anharmonicity induced localization. Whether one recognizes the concept of local modes in molecules, surface modes on surfaces, etc., it is the same theory of finite or infinite discrete systems that applies to all geometries.

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