

On the role of disorder in catalysis driven by discrete breathers

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A new mechanism of catalysis is discussed, which is based on the rate-promoting effect of large-amplitude anharmonic lattice vibrations, a.k.a. intrinsic localized modes or 'discrete breathers' (DBs), which can excite atoms at specific 'active sites' rather strongly, giving them energy far exceeding the energy of thermal vibrations for hundreds of oscillation periods. The DB-induced modulation of activation energies (free energy barriers between reactants and products) results in a drastic amplification of the reaction rates, which can be described by a simple analytical expression in the adiabatic limit. The striking site selectiveness of DB excitation dynamics in the presence of spatial (quenched) disorder makes these nonlinear vibrations viable candidates to play the role of 'active modes' in the catalytic process in various physical, chemical and biological systems.

Keywords: intrinsic localized modes, discrete breathers, heterogeneous catalysis, active sites.

1. Introduction

Catalysis is at the heart of almost every chemical transformation process, and a detailed understanding of the active species and their related reaction mechanism is of great interest [1]. Three main types of catalytic processes can be defined: heterogeneous, homogeneous and enzymatic.

In heterogeneous catalysis, catalysts are in a different phase from reactants. Normally, heterogeneous catalysis involves gas (or liquid) molecules interacting with solid surfaces at an atomic or nanometer scale. It is characterized by the presence of 'active sites' on the catalyst surface. In homogeneous catalysis, catalysts are in the same phase as reactants (*e.g.* dissolved in water), while the enzymatic catalysis (a.k.a. biocatalysis) has an intermediate character, because although enzymes and reactants are in the same phase, they have 'active sites' in their structure.

In this paper, we are interested mainly in heterogeneous catalysis (HC) and enzymatic catalysis (EC), which require 'active sites'. An important parameter of their kinetics is the activation energy, *i.e.* the energy required to overcome the reaction barrier. The lower is the activation energy, the faster the reaction rate, and so a catalyst may be thought as a means to reduce somehow the activation energy. Recently, it has been shown [2–4] that in a crystalline matrix, the activation energy may be reduced at some sites due to large-amplitude anharmonic lattice vibrations, a.k.a. intrinsic localized modes or 'discrete breathers' (DBs), that can be excited either thermally or by external driving, resulting in a drastic acceleration of the reaction rates. This allows one to suggest that DBs may be viable candidates for heterogeneous catalysts.

DBs are spatially localized large-amplitude vibrational modes in lattices that exhibit strong anharmonicity [5–8].

They have been successfully observed experimentally in various physical systems [8,9]. Studies of DBs in three-dimensional crystals by means of molecular dynamics (MD) simulations using realistic interatomic potentials include ionic crystals with NaCl structure [10,11], diatomic A3B crystals [12], graphene [13], semiconductors [14], metals [15,16] and layered insulators [17]. DBs in biopolymers such as proteins have been studied using the coarse-grained nonlinear network model (NNM) [18] as well as using intramolecular potentials fitted to reproduce thermally driven folding and unfolding, and mechanical manipulation experiments [19,20].

Presently the interest of researchers has shifted to the study of the role of DBs in solid state physics and their catalytic impact on the reaction rates in solids [2–4,9,15–18] and on the biological functions of biopolymers [19,20]. An important question in this respect concerns the mechanism that links DBs with 'active sites' of chemical and biological reactions. This question is addressed in the present paper.

The paper is organized as follows. In the next section, a rate theory of DB excitation in perfect crystals is developed, and dependence of the DB formation rate on the *energy gap* required for their excitation is derived. In section 3, a model for amplification of reaction rates by DBs is developed. In section 4, a striking *site selectiveness* of the DB formation in the presence of spatial disorder is discussed, which allows one to designate such sites as viable candidates for the 'active sites' in the catalytic process. The results are summarized in section 5.

2. DB excitation in crystals

The rate equation for the concentration of DBs with energy E , $C_{DB}(E, t)$ can be written as follows [2]

$$\frac{\partial C_{DB}(E, t)}{\partial t} = K_{DB}(E) - \frac{C_{DB}(E, t)}{\tau_{DB}(E)}, \quad (1)$$

where $K_B(E)$ is the rate of creation of DBs with energy $E > E_{\min}$ and $\tau_{DB}(E)$ is the DB lifetime. It has an obvious steady-state solution ($\partial C_{DB}(E, t)/\partial t=0$):

$$C_{DB}(E) = K_{DB}(E) \tau_{DB}(E), \quad (2)$$

In this section, we will consider breather formation by thermal activation in a crystal, and then discuss its application to disordered systems.

The exponential dependence of the concentration of high-energy light atoms on temperature in the MD simulations [12] gives evidence in favor of their thermal activation at a rate given by a typical Arrhenius law [7]

$$K_{DB}(E, T) = \omega_{DB} \exp\left(-\frac{E}{k_B T}\right), \quad (3)$$

where k_B is the Boltzmann constant and ω_{DB} is the natural (attempt) frequency that should be close to the DB frequency. The breather lifetime has been proposed in [7] to be determined by a phenomenological law based on two general principles. (i) DBs in a perfect crystal of two and three dimensions can be stable only above a given threshold energy E_{\min} . (ii) The lifetime of a breather grows with its energy as $\tau_{DB} = \tau_{DB}^0 ((E - E_{\min}) - 1)^z$, with z and τ_{DB}^0 being constants. From this it follows that at thermal equilibrium the DB energy distribution function $C_{DB}(E, T)$ and the mean number of breathers per site $n_{DB}(T)$ are given by

$$C_{DB}(E, T) = \omega_{DB} \tau_{DB} \exp\left(-\frac{E}{k_B T}\right), \quad (4)$$

$$\begin{aligned} n_{DB}(T) &= \int_{E_{\min}}^{E_{\max}} C_{DB}(E, T) dE = \\ &= \omega_{DB} \tau_{DB}^0 \frac{\exp\left(-\frac{E_{\min}}{k_B T}\right) \frac{E_{\max} - E_{\min}}{k_B T}}{\left(E_{\min}/k_B T\right)^{z+1}} \int_0^x y^z \exp(-y) dy \end{aligned}, \quad (5)$$

where $\Gamma(z+1, x) = \int_0^x y^z \exp(-y) dy$ is the incomplete gamma function. Equation (5) can be written as [2]

$$n_{DB} = \omega_{DB} \tau_{DB}^0 \frac{\exp(-E_{\min}/k_B T)}{\left(E_{\min}/k_B T\right)^{z+1}} \Gamma\left(z+1, \frac{E_{\max} - E_{\min}}{k_B T}\right), \quad (6)$$

It can be seen that the mean DB energy is higher than the average energy density (or temperature):

$$\langle E_{DB} \rangle = \frac{\int_{E_{\min}}^{E_{\max}} C_{DB}(E, T) E dE}{\int_{E_{\min}}^{E_{\max}} C_{DB}(E, T) dE} \xrightarrow{E_{\max} \gg E_{\min}} \frac{E_{\min}}{E_{\max} \gg E_{\min}} \rightarrow E_{\min} + (z+1)k_B T, \quad (7)$$

For example, according to [12], one has $E_{\min}/k_B T \approx 3$ and $\langle E_B \rangle \approx 5k_B T$, which gives us an estimate $z \approx 1$, i.e. for gap DBs in diatomic crystals, one has linear increase of the DB lifetime with energy.

3. Breather-induced catalyzing mechanism

In order to develop a mechanism for DB-based catalysis, one needs to select a reaction model, such as the classical Kramers model [26]. The model considers a Brownian particle moving in a symmetric double-well potential $U(x)$ (Fig.1), which is used very often as model for chemical reaction rate theory. The position of the particle represents the (free) energy of a system including the 'reaction site' in the phase space *energy-reaction coordinate*. The particle is subject to fluctuational forces induced by coupling to a heat bath. These forces cause transitions between the neighboring potential wells with a rate given by the celebrated Kramers rate, providing a theoretical basis for the Arrhenius law

$$R_K(E_0, T) = \omega_0 \exp(-E_0/k_B T) \quad (8)$$

where ω_0 is the natural attempt frequency (the curvature of the first energy minimum, i.e. the reactants) and E_0 is the height of the potential barrier separating the two stable states, corresponding to the reactants and products. Fluctuational forces acting on a Brownian particle imitate the interaction of a reaction site with a 'gas' of phonons, i.e. small amplitude harmonic oscillations of atoms.

A DB arising near the reaction site causes large-amplitude, quasi-periodic atomic oscillations, which can be described in terms of *time-periodic modulations* (driving) of the potential energy in the reaction described by Eq.(8). Namely, the double-well potential is tilted back and forth, thereby raising and lowering successively the potential barriers of the right and the left well, respectively, in an anti-phase manner (green and blue curves in Fig.1), such as

$$U(x, t) = U(x) - (V \cdot x/x_m) \cos(\Omega t), \quad (9)$$

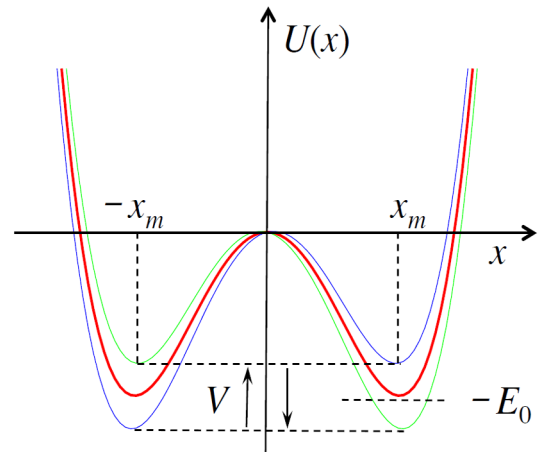


Fig. 1. Sketch of the double-well potential $U(x) = (1/4)bx^4 - (1/2)ax^2$ (red curve) The minima are located at $\pm x_m$, where $x_m = (a/b)^{1/2}$. These are stable states before and after reaction, separated by a potential 'barrier' with the height $E_0 = a^2/4b$ changing periodically within the V band. The green and blue curves represent the two maximally tilted energy landscapes.

If the driving frequency is much lower than the natural frequency, $\Omega \ll \omega_0$, one can use an ‘adiabatic’ approximation. This seems to be a realistic assumption in general. In proteins, for example it was found that as $\Omega \sim \omega_{DB} \sim 10^2 \text{cm}^{-1}$ [18]. This has to be compared with typical Debye frequencies of the order of hundreds of K, i.e. $\omega_0 \sim \omega_{DEBYE} \sim 10^4 \text{cm}^{-1}$. In this case, the reaction rate $\langle R_K \rangle$, averaged over times exceeding the driving period, has been shown to increase with respect to the ground value R_K according to the following expression [2]

$$\frac{\langle R_K \rangle}{R_K} \approx \frac{\Omega}{2\pi} \int_0^{2\pi/\Omega} \exp\left(\frac{V \cos(\Omega t)}{k_b T}\right) dt = I_0\left(\frac{V}{k_b T}\right), \quad (10)$$

where the amplification factor $I_0(x)$ is simply the zero order, modified Bessel function of the first kind. Note that the amplification factor is determined by the ratio of the driving amplitude V to temperature, and it does not depend on the driving frequency or the barrier height.

In a more detailed study of periodically driven stochastic systems by Jung [27], the amplification factor in the adiabatic approximation is given by the following integral

$$\frac{\langle R_K \rangle}{R_K} \approx A_F(V, E_0, T) = \frac{1}{2\pi} \int_0^{2\pi} \left[1 - \frac{3V}{16E_0} \sin(\varphi) \right] \times \exp\left[\frac{V}{k_b T} \sin(\varphi) - \frac{3V^2}{16E_0 k_b T} \sin^2(\varphi) \right] d\varphi, \quad (11)$$

which also depends on the barrier height. However, this dependence is rather weak for driving amplitudes low compared to the barrier height, as can be seen from Fig.2, which shows a comparison of the amplification factors given by Eqs.(10) and (11) at a typical value of the reaction barrier $E_0 = 1 \text{ eV}$.

One can see that, for $V = 0.3 E_0$, the relative difference between Eq.(10) and (11) is within 30% and it becomes significant only at $V \sim E_0$.

The adiabatic approximation is expected to be better in the case of soft type of nonlinearity (e.g. gap DBs in ionic crystals [10-12]) when the DB frequency is below the phonon band, and so one can expect the condition $\Omega < \omega_0$ to be fulfilled *a fortiori*. On the other hand, in semiconductors and metals [13–15] due to the hard type of non-linearity, the DB frequency lies above the Debye frequency (up to ~50%) and so the driving frequency can be slightly above the attempt frequency of the reaction. However, numerical results [27] show that the adiabatic approximation is only about 10% off the true result in the case $\Omega \approx \omega_0$. Although the reaction amplification factor decreases with increasing driving frequency in this region, the reduction can be significant only for $\Omega \gg \omega_0$ while it has the same order of magnitude as the adiabatic value for $\Omega \geq \omega_0$, which is expected to be the case even for the hard type DBs.

Equations (10), (11) can be written in the following form

$$\langle R_K \rangle = \omega_0 \exp\left(-E_a^{DB} / k_b T\right), \quad (12)$$

where the *DB-modified activation energy* is given by

$$E_a^{DB} = E_0 - k_b T \ln \left\{ I_0 \left(\frac{V}{k_b T} \right) \right\}, \quad (13)$$

$$E_a^{DB} = E_0 - k_b T \ln \left\{ A_F(V, E_0, T) \right\}. \quad (14)$$

It decreases with increasing driving amplitude and decreasing temperature as shown in Fig.3.

The main conclusion here is that the DB-induced periodic driving can amplify the average reaction rate drastically if the ratio $V/k_b T$ is high enough, as it is demonstrated in Fig.2. That is what is expected to be the case in the reaction site interacting with a nearby DB, since MD simulations using realistic interatomic potentials of various materials show that a typical deviation of the potential energy of atoms within a DB is of the order of several fractions of eV [10–16].

4. DBs in spatially disordered systems

In regular lattices, usually, a finite energy threshold has to be overcome in order to create a DB, which is reflected in Eqs.(6,7). Generally, depending on the spatial dimension and type of nonlinearity in the inter-particle potentials, a finite threshold may, or may not, exist [19]. In the context of spatially disordered systems, such a question has to be formulated not only in terms of the existence of a gap, but also in terms of its nature. It is important to stress that in an ordered system the bifurcation of the nonlinear edge mode marks a symmetry breaking, the emerging DB mode being exponentially localized, while the edge linear mode has an extended pattern. In topologically disordered systems, sites

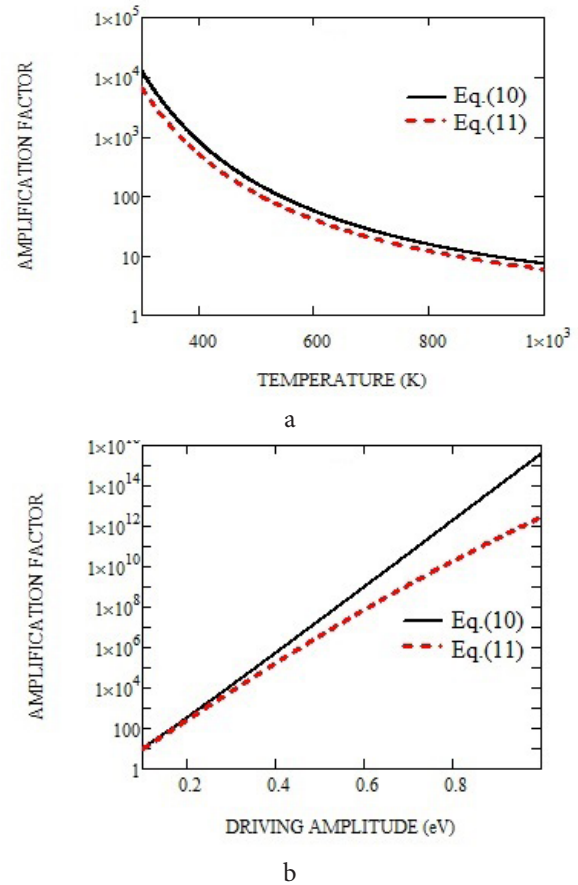


Fig. 2. Amplification factor for the escape rate of a thermalized Brownian particle from a periodically driven potential well at different temperatures and driving amplitudes at the reaction barrier $E_0 = 1 \text{ eV}$. (a) $V = 0.3 \text{ eV}$; (b) $T = 300 \text{ K}$.

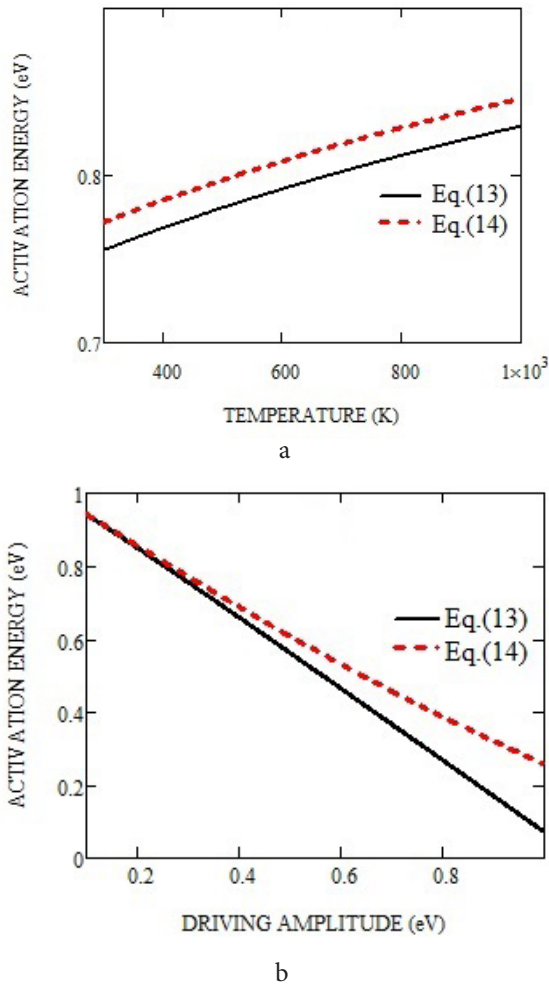


Fig. 3. DB-modified activation energy vs. temperature (a) and driving amplitude (b) at the reaction barrier $E_0 = 1$ eV. (a) $V = 0.3$ eV; (b) $T = 300$ K.

are not equivalent and band-edge modes are intrinsically localized in space, different modes having their largest displacement in different regions of the structure. Hence, different families of DBs may exist, localized at different sites and approaching different edge normal modes for vanishing amplitudes [18].

Thus, in contrast to perfect crystals, which produce DBs homogeneously, there is a striking *site selectiveness* of energy localization in the presence of spatial disorder, which will be demonstrated below in two examples.

5. Biopolymers

Biopolymers such as proteins and nucleic acids fold into complex three-dimensional structures (Fig.4), whose shape is strictly connected to their biological function. Proteins under physiological conditions are immersed in a thermal bath and therefore exhibit random thermal fluctuations. However, the biological function of a given biopolymer is often closely related to a particular kind of motion, typically involving large-amplitude low-frequency collective modes [21] and possibly also DB-like large-scale vibrations at higher frequencies [18,20].

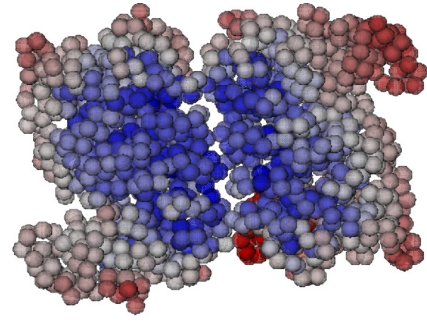


Fig. 4. Structure of dimeric citrate synthase (PDB code 1IXE). Only α -carbons are shown, as spheres in a color scale corresponding to the crystallographic B-factors, from smaller (blue) to larger (red) fluctuations.

While studying thermal excitation of DBs in protein clusters, Piazza and Sanejouand [18] have found that as a sheer consequence of disorder, a non-zero energy gap for exciting a DB at a given site may disappear at some special sites. At such sites, a small subset of linear edge modes acts as accumulation points, whereby DBs can be continued to arbitrary small energies, while unavoidably approaching one of such normal modes. Concerning the structure–dynamics relationship, a thorough analysis performed on a large dataset of enzyme structures has shown that the regions where DBs form easily (zero or small gaps) are generically the stiffest portions of the protein scaffold, characterized by large local

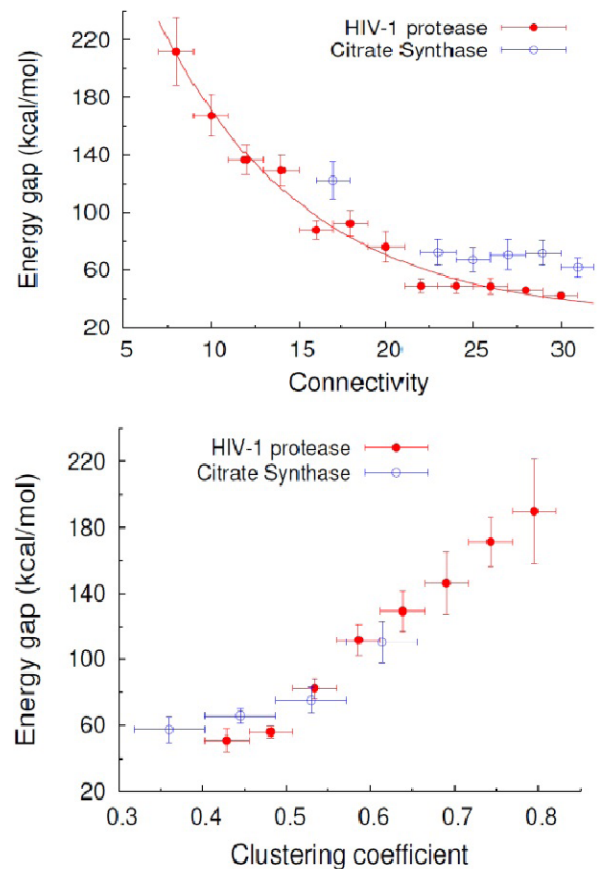


Fig. 5. DB energy gaps versus connectivity and clustering coefficient in HIV-1-protease (PDB 1A30) and Citrate Synthase (PDB 1IXE). The solid line in the top panel is a guide to the eye [19].

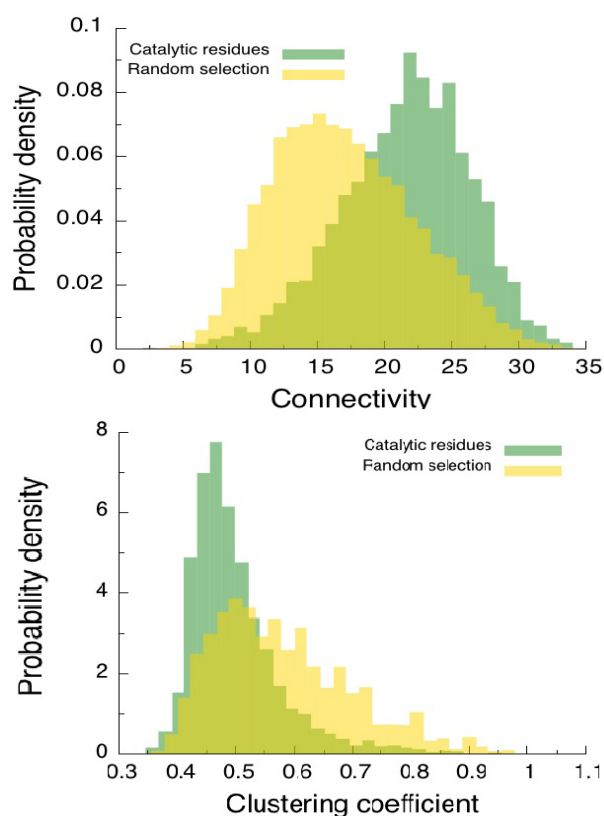


Fig. 6. Distribution of connectivities and clustering coefficients of aminoacids for enzymes within the Catalytic Site Atlas database [22]. Comparison of the subset of residues involved in the catalytic activity with a subset of generic aminoacids, randomly selected within the database with the same proportion of chemical types as present in the catalytic sub-set.

connectivity and weak local clustering, as demonstrated in Figs.5 and 6.

These results point to the existence of specific spatial selection rules that govern the range of existence/stability of a DB located at a given site. Remarkably, catalytic sites, where the reactant molecule binds to the enzyme, thus initiating the catalytic cycle, are generically found in highly stiff regions in the proteins [18,23]. These are precisely the hot-spots where DB excitation is facilitated, as the gap vanishes around such sites and energy can be easily collected at [18] and/or funneled [24] to such regions by means on nonlinear mechanisms, that can further lead to the stabilization of such energetic fluctuations where needed over a large number of vibrational cycles.

In view of the above discussion, it is thus tempting to speculate that DB excitation might play a pivotal role in promoting enzyme catalysis, as it has been already suggested [25].

6. Metal nanoparticles

Zhang and Douglas [28] provided another example of the role of disorder in energy localization mechanisms by investigating interfacial dynamics of Ni nanoparticles at high temperatures exceeding 1000 K. They discovered a string-like

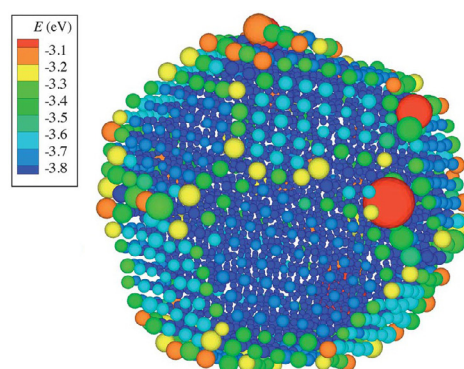


Fig. 7. Atomic configuration of a Ni nanoparticle of 2899 atoms at $T = 1000$ K. The atoms are colored based on the potential energy and their size is proportional to Debye-Waller factor $\langle u^2 \rangle$. Both potential energy and $\langle u^2 \rangle$ are time averaged over a 130 ps time window, corresponding to the time interval during which the strings show maximum length. Reproduced from Ref.[28] with permission from The Royal Society of Chemistry.

collective motion of surface atoms with energies in the eV range, *i.e.* exceeding the average lattice temperature by an order of magnitude (Fig.7). One of the most intriguing observations of this study was the propagation of *breather-like excitations* along the strings, providing a possible mechanism for driving such correlated string-like atomic displacement movements. Note that regions of high mobility string-like motion are concentrated in filamentary grain boundary like domains that separate regions having relatively strong short-range order (Fig.8). The authors conclude that these dynamic structures might be of crucial significance in *relation to catalysis*.

7. Conclusions and outlook

Persistent spatially localized vibrations of nonlinear origin known as discrete breathers (DBs) can be excited generically in many-body nonlinear systems. Remarkably, in heterogeneous structures, DBs preferentially localize at

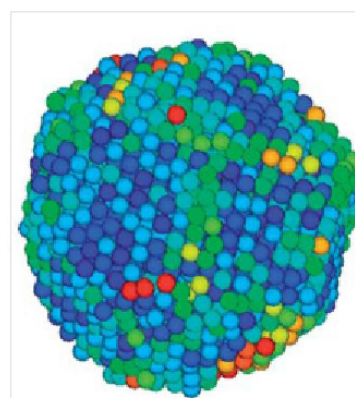


Fig.8. Map of the local Debye-Waller factor showing the heterogeneity of the atomic mobility at a temperature of 1450 K. Regions of high mobility string-like motion are concentrated in filamentary grain boundary like domains that separate regions having relatively strong short-range order. Reproduced from Ref.[28] with permission from The Royal Society of Chemistry.

sites with specific structural features, typically in the stiffest and most connected neighbourhoods. In enzymes these are invariably located in close contact with the active sites of the enzymes, where the catalytic action is initiated.

The striking *site selectiveness* of DB formation in the presence of spatial disorder may allow one in principle to identify specific *hot-spot* sites in heterogeneous structures to predict ‘*active sites*’ of catalytic process in various chemical [1], physical [4,17,28], biological [18,20,21] and even nuclear [29] systems. Remarkably, DBs may constitute a universal means for realizing efficient rate-promoting vibrations with fine-tuned structural precision, able to lower free-energy barriers for chemical reactions by persistent modulation of the corresponding activation energies.

An important consequence of our reasoning is that it may indicate a way of *engineering* the active environment based on MD modeling of DB excitation dynamics in nanoparticles and disordered structures of various types.

In such systems, instead of thermodynamic considerations leading to Eq.(3) one needs to consider the kinetics of normal mode instability leading to the DB creation. This fundamental problem extends beyond the purpose of the present communication and will be addressed elsewhere.

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