Discrete Breathers in Hydrogenated Metals:
Atomistic Simulations and Applications to the Rate Theory

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• DBs/ILMs in metals
• DB role in catalysis at high T (violation of Arrhenius low)
• DB role in catalysis at low T (quantum tunneling)
• MD simulations in Ni, Pd, Ni-H, Pd-H crystals and Pd nanoclusters (3d DB)
The distance between the nearest atoms in Ni at room temperature is \( r_0 = 2.49 \, \text{Å} \) and longitudinal sound velocity is \( v_l = 5266 \, \text{m/s} \). These values give \( \tilde{K}_2 = 2.75 \, \text{eV/Å}^2 \) (as expected, \( \tilde{K}_2 > K_2 \)) and \( \tilde{\kappa} \approx 1.2 \). The distance \( r_0 \) increases...
Standing DB in bcc Fe: $d_0=0.3$ Å

D. Terentyev, V. Dubinko, A. Dubinko (2013)
DB along [111] direction in bcc Fe at T=0K

Initial conditions:

\[ x_{n-2} = +0.2 \quad x_{n-1} = -0.2 \quad x_n = +0.4 \quad x_{n+1} = -0.4 \quad x_{n+2} = +0.2 \quad x_{n+3} = -0.2 \]

Boundary conditions: periodic

It is seen from the visualization, that the DB has been generated from the initial anti-phase displacements of 6 atoms.
Moving DB in bcc Fe: $d_0=0.4$ Å, $E=0.3$ eV
D. Terentyev, V. Dubinko, A. Dubinko (2013)
DB in bulk Pd 3D lattice (2017)

LAV Time Period = 0.1292 ps
LAV frequency = 7.7399 THz

The DB frequency lies above the phonon vibration spectrum.
Effective ‘temperature’ of DB (#1100) and lattice (#1095) atom in fcc Pd lattice
DB effect (1): periodic in time modulation of the potential barrier height
Reaction-rate theory with account of the crystal anharmonicity

\[ R_K = \frac{\omega_0}{2\pi} \exp\left[-\frac{E_0}{k_B T}\right] \leq \text{Kramers rate} \]

\[ U(x,t) = U(x) - (V \cdot x / x_m) \cos(\Omega t) \]

Kramers rate is amplified by:

\[ I_0\left(\frac{V_m}{k_B T}\right) - \text{Bessel function} \]
Low temperature reconstructive transformation of muscovite

K$_2$[Si$_6$Al$_2$]$^{IV}$[Al$_4$]$^{VI}$O$_{20}$(OH)$_4$

Disilicate of Lutetium Lu$_2$Si$_2$O$_7$

$E_a > 1$ eV

300° C, 3 days

About 36% of muscovite is transformed, which is $10^4 - 10^5$ times faster than by Arrhenius law:

At T = 1000° C, 3 days

At T = 300° C, 10$^3$ years

$\dot{R}_K = v \exp(-E_a/k_BT)$
Transformation rate of muscovite with account of DB statistics Dubinko et al (2011)

\[
\left\langle \dot{R} \right\rangle_B = \hat{R}_K \left( \int_{E_{\text{min}}}^{E_{\text{mod}}} f_B(E) I_0(E) dE + \int_{E_{\text{mod}}}^{E_{\text{max}}} f_B(E) I_0(E_r) dE \right)
\]

where

- \( E_{\text{mod}} = \begin{cases} E_{\text{max}} & \text{if } E_{\text{max}} \leq E_a \\ E_a & \text{if } E_a < E_{\text{max}} \end{cases} \)

- \( E_{B,\text{max}} = 1 \text{ eV} \)

Kramers rate:

\[
\hat{R}_K^e = \nu \exp \left( - \frac{E_a}{k_b T} \right)
\]
How extend this concept to include Quantum effects, Tunneling?
Tunneling: Numerical solution of Schrödinger equation

Stationary: $t_{\text{Kramers}} \sim 10^5$ cycles at $V_{\text{barrier}} = 12E_0$

Time-periodically driven: $\Omega = 1.5 \omega_0$, $g = 0.2$

The Kramers theory is extended in order to take into account both the action of the thermal and zero-point oscillation (ZPO) energy.

\[ R_K = \frac{\omega_0}{2\pi} \exp \left[- \frac{E_0}{D(T)}\right] \]

\[ D(T) = E_{ZPO} \coth \left( \frac{E_{ZPO}}{k_BT} \right) \approx \begin{cases} E_{ZPO}, & T \to 0 \\ k_BT, & T \gg E_{ZPO}/k_B \end{cases} \]

- temperature is a measure of thermal noise strength

\[ E_{ZPO} = \frac{h\omega_0}{2} \] - ZPO energy is a measure of quantum noise strength
When we heat the system we increase temperature, i.e. we increase the *thermal* noise strength.

Can we increase the *quantum* noise strength, i.e. ZPO energy?
Stationary harmonic potential

\[ \langle E \rangle_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) \]

\[ E_{ZPO} = \frac{\hbar \omega_0}{2} \]
Time-periodic modulation of the double-well shape changes (i) eigenfrequency and (ii) position of the wells.
Parametric resonance with time-periodic eigenfrequency $\Omega = 2\omega_0$

\[
\frac{ih}{\partial t} \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{m\omega^2(t)}{2} x^2 \psi
\]

Schrödinger equation

\[
\psi(x_0, t_0 = 0) = \frac{1}{\sqrt{4\pi\sigma_0}} \exp\left(-\frac{x_0^2}{4\sigma_0}\right)
\]

Initial Gaussian packet

$\sigma_0 = \frac{\hbar}{2m\omega_0}$

Parametric regime $\Omega = 2\omega_0$:

\[
\dot{x} + \omega_0^2 \left[1 - g \cos\left(2\omega_0 t\right)\right] x = 0
\]

$g << 1$ – modulation amplitude

\[
\sigma_x(t) = \sigma_0 \cosh\left(\frac{g\omega_0 t}{2}\right) \left[1 + \tanh\left(\frac{g\omega_0 t}{2}\right) \sin(2\omega_0 t)\right]
\]

dispersion

ZPO energy:

\[
E_{ZPO}(t) = \frac{h\omega_0}{2} \cosh\frac{g\omega_0 t}{2}
\]

ZPO amplitude:

\[
\Lambda_{ZPO}(t) = \sqrt{\frac{\hbar}{2m\omega_0}} \cosh\frac{g\omega_0 t}{2}
\]
Non-stationary harmonic potential with time-periodic eigenfrequency $\Omega = 2\omega_0$

$$\Lambda_{ZPO}(t) = \sqrt{\frac{\hbar}{2m\omega_0}} \cosh \frac{g\omega_0 t}{2}$$

$$E_{ZPO}(t) = \frac{\hbar\omega_0}{2} \cosh \frac{g\omega_0 t}{2}$$
Escape rate in the modified Kramers theory with account of parametric driving of the well eigenfrequency \( \Omega = 2\omega_0 \)

\[ E_0 = 1 \text{ eV} \text{ – the well depth; } \quad g = 0.1 \text{ – the modulation amplitude} \]
Non-stationary harmonic potential with time-periodic shifting of the well position at $\Omega = \omega_0$

$$\langle E \rangle = \frac{\hbar \omega_0}{2} + \frac{(g_A A_{ZPO})^2}{8} m \omega_0^2 \left[ \omega_0^2 t^2 + \omega_0 t \sin 2 \omega_0 t + \sin^2 \omega_0 t \right]$$

$$\lambda(t) = \frac{g_A A_{ZPO}}{2} \omega_0 t \left( \cos \omega_0 t - \frac{\sin \omega_0 t}{\omega_0 t} \right)$$
Escape rate in the modified Kramers theory with account of parametric driving of the well position at $\Omega = \omega_0$

$$R_K = \frac{\omega_0}{2\pi} \exp\left[-(E_0 - \langle E \rangle)/D(T)\right]$$

$$D(T) = \frac{\hbar \omega_0}{2} \coth\left(\frac{\hbar \omega_0}{2k_B T}\right)$$

$E_0 = 1 \text{ eV} - \text{well depth}; \quad g_A = 0.5 - \text{modulation amplitude}$
**Tunneling:** Numerical solution of Schrödinger equation

Stationary: $t_{\text{Kramers}} \approx 10^5$ cycles at $V_{\text{barrier}} = 12E_0$

Time-periodically driven: $\Omega = 1.5 \omega_0$, $g = 0.2$
DBs at finite T in diatomic crystals
Gap DBs in NaCl type lattices, Dmitriev et al (2010)

NaCl-type $M_H/M_L = 10$ at temperatures $T = (a) 0$, (b) 155, (c) 310, and (d) 620 K

DOS for $\text{PdD}_{0.63}$ and $\text{PdH}_{0.63}$: $M_H/M_L = 50$; 100 D pressure of 5 GPa and $T=600$ K
MD modeling of LAVs in NiH and PdH crystals
Visualization of the Pd(Ni)H fcc Lattice (NaCl type)
**NiH lattice**

The following potential was used for Ni lattice modeling in **LAMMPS** package:

<table>
<thead>
<tr>
<th>Material</th>
<th>File with potential used</th>
<th>The link to the corresponding publication in the literature</th>
</tr>
</thead>
</table>
Density Of States of NiH at 0 K

DOS NiH

$g(v)$ vs $v$ (THz)
1 H atom displaced along [110] in NiH at T=0K
1 H atom displaced along $\langle 110 \rangle$ in NiH at $T=0K$

T=0.5 ps, Frequency = 20THz (inside the optical band)
Discrete Breather in the 3d NiH Lattice at 0 K

1 atom H is displaced along <100> at 0.8 Å. Initial velocity = 0.

DB frequency = 29 THz
DB amplitude = 0.9 Å
Lattice constant = 3.5 Å

The Embedded Atom Method has been used

\[ \rho_i = \sum_j f_j(r_{ij}) \]
\[ E = \sum_{i<j} V_{ij}(r_{ij}) + \sum_i F_i(\rho)_i \]

DB frequency lies near the upper edge of the phonon band
2 H atoms [100] and [-100] in NiH at T=0K
2 H atoms [100] and [-100] in NiH at T=0K
2 H atoms [100] and [-100] in NiH at T=0K

DB frequency = 33 THz (above the optic band)
DB amplitude = 0.8Å
Lattice constant = 3.5Å
Do DBs exist at finite $T$ ?
Visualization of the PdH fcc Lattice Oscillations at $T=100$ K
Visualization of the PdH fcc Lattice Oscillations at $T=1000K$
Gap DBs in diatomic crystals at elevated temperatures

A$_3$B type crystals $M_H/M_L = 10$

In NaI and KI crystals Hizhnyakov et al has shown that DB amplitudes along <111> directions can be as high as 1 Å, and $t^*/\Theta \sim 10^4$

Lifetime and concentration of high-energy light atoms increase exponentially with increasing T

$K_{B,n}^*/\bar{K} \approx 5.1$

$t^*/\Theta \approx 70$ $\bar{K} = 0.1eV \geq 1000K$
Morse pairwise potentials have been used for MD modeling

FIG. 5. (Color online) Characteristics of high-energy atoms in the crystal with atomic weight ratio $M_B/M_A = 0.10$. Rows correspond to five energies, $\bar{K} = \{0.025, 0.05, 0.075, 0.1, 0.125\}$ eV. (a)–(e) Relative energy of heavy atoms in high-energy state, $K_{A,n}^*/\bar{K}$, as a function of lifetime of this state, $t^*/\Theta$; (a′)–(e′) same as in (a)–(e), but for light atoms; (a′′)–(e′′) concentrations of high-energy heavy atoms, $C_A^*$ (thick line), and high-energy light atoms, $C_B^*$ (thin line), as functions of their lifetime, $t^*/\Theta$. The ordinate is given in logarithmic scale.

Morse pairwise potentials have been used for MD modeling.
NiH lattice (not deformed) at different T

As the temperature rises, low frequencies begin to predominate, which is apparently connected with the destruction of the hydride lattice and the increase in the mean free path of hydrogen atoms, which begin ‘free motion’ inside the lattice.
Compressed (on 10%) PdH lattice at T=620K and T=1000K

With increasing T the phonon density shifts somewhat to the high-frequency region but no ‘shoulder’ appears in the gap.
Compressed (on 10%) NiH lattice at T=20K and T=1240K

As the temperature rises, low frequencies begin to predominate, which is apparently connected with the destruction of the hydride lattice and the increase in the mean free path of hydrogen atoms, which begin the ‘free motion’ inside the lattice.
NiH MD modeling in LAMMPS package

T = 1160 K

Number of High-Energy States vs. t/T
NiH lattice at $T=1160\text{K}$. High energy oscillations

Data for some arbitrary H atom in the Lattice

NiH MD modeling in \textbf{LAMMPS} package
NiH MD modeling in LAMMPS package
Magic Clusters

*magic clusters* (rus. кластеры, магические) — clusters of certain ("magic") sizes, which, due to their specific structure, have higher stability as compared to clusters of other sizes.

Number of atoms in the icosahedral cluster

\[ n = (2N + 1) + 10 \sum_{k=1}^{N} k^2 \]

\[ n = 13, 55, 147, 309, 561 \]

Mass spectrum of carbon clusters produced by laser evaporation of graphite. The highest peak corresponds to \( \text{C}_{60} \) fullerene molecules, and the less intensive peak represents \( \text{C}_{70} \) molecules.
Quasi-crystaline Pd cluster

Cluster of 13 Pd atoms with quasi-crystalline 5th order symmetry axis.

E0=0.1eV
3d breather in a Magic cluster of 55 Pd atoms with quasicrystalline $5^{th}$ order symmetry axis.
Initial conditions:
at the initial time moment all particles have zero displacements from equilibrium positions.

Atom #1 has initial kinetic energy $1.5\text{eV}$ in [00-1] direction.

Atom #12 has initial kinetic energy $1.5\text{eV}$ in [001] direction.

Boundary conditions: free surfaces of cluster
Dynamics of the icosahedral cluster of 55 Pd atoms

It is seen from the visualization, that Localized Anharmonic Vibration is generated. The observed LAV in the atomic cluster represents the coherent collective oscillations of Pd atoms along quasi-crystalline symmetry directions.
If the initial energy, given to cluster is large enough (greater than the cohesive energy) then the cluster is destroyed after a certain period of time (~ ps).
Conclusions and outlook

New mechanism of catalysis in solids is proposed, based on time-periodic driving of the potential landscape induced by DBs.

At high T, DBs may result in effective lowering of the reaction activation barrier.

At low T, DBs may result in increasing energy of Zero Point Vibrations enhancing the tunneling through the potential barrier

Outstanding problems:

Existence and properties of LAV at elevated temperatures

Account of quantum effects in MD/DFT at low temperatures

Experimental verification of the proposed concept
Publications

THANK YOU FOR YOUR ATTENTION!
\[ \langle E \rangle_{\text{theor}}(t) \approx \hbar \omega_0 \left( n + \frac{1}{2} \right) \cosh \frac{g \omega_0 t}{2} \]

\[ g \ll 1 \]

\[ \langle E \rangle_{\text{num}}(t) = \frac{\hbar \omega_0}{2} \left( n + \frac{1}{2} \right) \left[ \frac{\dot{Y}^2 + \omega_0^2 \dot{Z}^2}{\omega_0^2} + \frac{\omega^2(t)}{\omega_0^2} (Y^2 + \omega_0^2 Z^2) \right] \]

General case: \( n = 0, 1, 2, \ldots \)

\[
\begin{align*}
g &= 0.1, \quad n = 0 \\
\end{align*}
\]

\[
\begin{aligned}
\dot{Y}(t) + \omega^2(t)Y(t) &= 0 \\
\dot{Y}(0) &= 0, \quad Y(0) = 1 \\
\dot{Z}(t) + \omega^2(t)Z(t) &= 0 \\
\dot{Z}(0) &= 1, \quad Z(0) = 0 \\
\omega^2(t) &= \omega_0^2 \left[ 1 - g \cos(2\omega_0 t) \right]
\end{aligned}
\]