Intrinsic Point Defects: Vacancies

- Energy and entropy of vacancy formation
- Configurational and thermal entropy
- Equilibrium vacancy concentration
- Divacancies and vacancy aggregates
- Sources and sinks of vacancies
- Time to reach equilibrium
- Methods of probing vacancy concentration
- Vacancies and thermal expansion
- Vacancies and heat capacity

References:
Allen & Thomas, Ch. 5, pp. 249-257
Kelly, Groves, Kidd, Ch. 9, 261-289
Swalin, Chs. 11 and 12, pp. 259-277
Equilibrium vacancy concentration

A distinctive characteristic of point defects is that they can be present at substantial concentrations under conditions of thermodynamic equilibrium. They are sometimes called “thermodynamically reversible defects” - they can be controlled by thermodynamic parameters - $T$ and $P$.

Thermodynamic equilibrium under conditions of constant $P$ and $T$: $G = H - TS \rightarrow \text{min}$

To find the equilibrium vacancy concentration, we have to find the change in $G$ as a result of the introduction of $n$ vacancies into a crystal with $N$ lattice sites:

$$\Delta G = G^n - G^0 = \Delta H_f^n - T\Delta S^n$$

$$\Delta H_f^n = n\Delta h_f$$

$\Delta h_f$ is the enthalpy of vacancy formation - lattice relaxation makes it substantially (~3-4 times) smaller than the heat of vaporization

E.g., for Au: $\Delta h_f \approx 0.97$ eV, latent heat of vaporization $\Delta h_s \approx 2.6$ eV, cohesive energy $E_c \approx 3.8$ eV

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What is entropy?

“Any method involving the notion of entropy, the very existence of which depends on the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension.”

Willard Gibbs

Introduced in the 2\textsuperscript{nd} law of thermodynamics to quantify irreversibility of a process:

2\textsuperscript{nd} Law: There exist a state function, the entropy $S$, which for all reversible processes is defined by $dS = \delta q_{rev}/T$ and for all irreversible processes is such that $dS > \delta q/T$, or in general, $dS \geq \delta q/T$.

The entropy of a system plus its surroundings (together forming “the universe” – an isolated system - $\delta q = 0$) never decreases and increases in any irreversible process.

Physical interpretation of entropy: In statistical thermodynamics entropy is defined as a measure of randomness or disorder.

How to quantify “disorder”?

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What is entropy?

How to quantify “disorder”? - microstates and macrostates

A macroscopic state of a system can be described in terms of a few macroscopic parameters, e.g. $P$, $T$, $V$. The system can be also described in terms of microstates, e.g. for a system of $N$ particles we can specify coordinates and velocities of all atoms.

The 2$^{nd}$ law can be stated as follows: The equilibrium state of an isolated system is the one in which the number of possible microscopic states is the largest.

$$S = k_B \ln \Omega$$

$\Omega$ is the number of microstates, $k_B$ is the Boltzmann constant (it was first introduced in this equation), and $S$ is the entropy.

The entropy is related to the number of ways the microstate can rearrange itself without affecting the macrostate.

The 2$^{nd}$ law can be restated again: An isolated system tends toward an equilibrium macrostate with maximum entropy, because then the number of microstates is the largest.
**Configurational entropy and thermal (vibrational) entropy**

**Vibrational entropy \( S_v \):** Entropy associated with lattice vibrations (the number of microstates \( \Omega \) can be thought as the number of ways in which the thermal energy can be divided between the atoms).

The vibrational entropy of a material increases as the temperature increases and decreases as the cohesive energy increases.

The vibrational entropy plays important role in many polymorphic transitions. With increasing \( T \), the polymorphic transition is from a phase with lower \( S_v \) to the one with lower vibrational frequencies and higher \( S_v \), e.g. fcc \( \rightarrow \) bcc (\( \Delta H_{tr} > 0 \) can be compensated by \(-T\Delta S < 0 \)).

**Configurational entropy \( S_c \):** Entropy can be also considered in terms of the number of ways in which atoms themselves can be distributed in space, e.g. entropy of mixing in quasi-chemical model.

\[ T_1 < T_2 \quad \Rightarrow \quad S_v \uparrow \]

\[ T_1 = T_2 \quad \Rightarrow \quad S_c \uparrow \]
Equilibrium vacancy concentration

\[ \Delta G = G^n - G^0 = \Delta H_f^n - T \Delta S^n \]

\[ \Delta H_f^n = n \Delta h_f \quad \Delta S^n = \Delta S_c^n + \Delta S_v^n \quad \Delta S_v^n = n \Delta s_v \]

\( \Delta s_v \) is change in the vibrational entropy due to the introduction of one vacancy - related to changes in the vibrational frequencies of atoms surrounding the vacancy

\[ \Delta G = G^n - G^0 = n(\Delta h_f - T \Delta s_v) - T \Delta S_c^n \]

\[ \Delta S_c^n = S_c^n - S_c^0 \quad S_c^n = k_B \ln(\Omega_n) \]

\( n = 0 : S_c^0 = k_B \ln(1) = 0 \)

\( n = 1 : S_c^1 = k_B \ln(N) \)

\( n = 2 : S_c^2 = k_B \ln[1/2 N(N-1)] \gg S_c^1 \)

\( n = 3 : S_c^2 = k_B \ln[1/6 N(N-1)(N-2)] \gg S_c^2 \)

… in general, the number of distinct configurations for \( n \) vacancies is

\[ \frac{1}{n!} N(N-1)(N-2)...(N-n+1) = \frac{N!}{n!(N-n)!} \]
Equilibrium vacancy concentration

$$S_c^n = k_B \ln \frac{N!}{n!(N-n)!}$$

$$\Delta G = n(\Delta h_f - T\Delta s_v) - T\Delta S_c^n$$

Equilibrium concentration of vacancies can be found from:

$$\left. \frac{\partial \Delta G}{\partial n} \right|_{n=n_{eq}} = 0$$

Let’s first consider \( \frac{\partial S_c^n}{\partial n} \) using Stirling formula for big numbers: \( \ln N! \approx N \ln N - N \)

$$\frac{\partial S_c^n}{\partial n} = k_B \frac{\partial}{\partial n} \left\{ \ln N! - \ln n! - \ln (N-n)! \right\} \approx k_B \frac{\partial}{\partial n} \left\{ N \ln N - N - n \ln n + n - (N-n) \ln (N-n) + (N-n) \right\} =$$

$$k_B \frac{\partial}{\partial n} \left\{ N \ln N - n \ln n - (N-n) \ln (N-n) \right\} = k_B \left\{ - \ln n - 1 + \ln (N-n) - \frac{N-n}{N-n}(1) \right\} = k_B \ln \left( \frac{N-n}{n} \right) =$$

$$k_B \ln \left( \frac{N-n}{n} \right) \approx -k_B \ln \left( \frac{n}{N} \right)$$

$$\left. \frac{\partial \Delta G}{\partial n} \right|_{n=n_{eq}} = \frac{\partial}{\partial n} \left\{ n(\Delta h_f - T\Delta s_v) - TS_c^n \right\} \bigg|_{n=n_{eq}} = \Delta h_f - T\Delta s_v + k_B T \ln(n_{eq}/N) = 0$$

$$\frac{n_{eq}}{N} = \exp \left( \frac{\Delta s_v}{k_B} \right) \exp \left( -\frac{\Delta h_f}{k_B T} \right)$$
The equilibrium vacancy concentration is defined by the balance between $n(\Delta h_f - T \Delta s_v)$ and $-T \Delta s^{n}_c$

$$\frac{\partial (-T \Delta s^{n}_c)}{\partial n} \bigg|_{n \to 0} \approx k_B T \ln \left( \frac{n}{N} \right) \bigg|_{n \to 0} \to -\infty$$

steep dependence of the entropy term at small $n/N$ → defect-free crystals do not exist (nanoparticles?)

$$-T \Delta s^{n}_c = -k_B T \ln(\Omega_n)$$
Energy of vacancy formation $\Delta h_f$

Rough estimation of $\Delta h_f$ based on an assumption that cohesive energy $E_c$ is equal to the sum of bond energies between adjacent atoms.

By moving an atom to the surface: (1) bonds of an atom that was at the vacancy site are broken (adding $E_c$), (2) some of the bonds of the atoms surrounding the vacancy are broken (adding another $E_c$), (3) atom is moved to the surface and restores some of the bonds (removing $E_c$), (4) atoms around the vacancy are relaxed (reducing energy by $\Delta E_R$):

$$\Delta h_f = 2E_c - E_c - R = E_c - \Delta E_R$$

The accuracy of experimental and theoretical evaluation of $\Delta h_f$ is limited, with substantial variability in reported data.

<table>
<thead>
<tr>
<th>material</th>
<th>Al</th>
<th>Au</th>
<th>Cu</th>
<th>Ni</th>
<th>$\alpha$-Fe</th>
<th>W</th>
<th>Si</th>
<th>Ar</th>
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<tbody>
<tr>
<td>$\Delta h_f$ (eV)$^a$</td>
<td>0.68</td>
<td>0.97</td>
<td>1.22</td>
<td>1.6</td>
<td>1.5</td>
<td>3.7</td>
<td>2.1$^c$ - 3.6$^d$</td>
<td>0.06-0.09$^e$</td>
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<tr>
<td>$E_c$ (eV)$^b$</td>
<td>3.39</td>
<td>3.81</td>
<td>3.49</td>
<td>4.44</td>
<td>4.28</td>
<td>8.9</td>
<td>4.63</td>
<td>0.08</td>
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<tr>
<td>$T_m$ (K)$^a$</td>
<td>933</td>
<td>1336</td>
<td>1356</td>
<td>1726</td>
<td>1808</td>
<td>3653</td>
<td>1687</td>
<td>84</td>
</tr>
</tbody>
</table>

$^a$ Allen & Thomas
$^b$ Kittel, *Introduction to Solid State Physics*
$^c$ Bracht et al., PRL 91, 245502, 2003
$^d$ Dannefaer, Mascher, Kerr, PRL 56, 2195, 1986
$^e$ Schwalbe, PRB 14, 1722, 1976

$\Delta h_f$ is mostly the energy of electron density rearrangement around the vacancy, with the elastic energy making relatively small contribution.
Vibrational entropy of vacancy formation $\Delta s_v$

$\Delta s_v$ is local and associated with the introduction of a single vacancy, which is different from $\Delta S_c$ that depend on the total number of defects in the crystal.

$\Delta s_v$ can be roughly estimated by considering Einstein model of a solid proposed to explain low-T behavior of heat capacity (deviation from Dulong – Petit law).

Einstein model: a solid is as an ensemble of independent quantum harmonic oscillators all vibrating at the same frequency $\nu$. Quantum theory gives the energy of $i^{th}$ level of a harmonic quantum oscillator as $\varepsilon_i = (i + \frac{1}{2}) \hbar \nu$ where $i = 0, 1, 2, \ldots$, and $\hbar$ is Planck’s constant.

For a quantum harmonic oscillator the Einstein-Bose statistics must be applied (rather than Maxwell-Boltzmann statistics and equipartition of energy for classical oscillators). For temperatures higher than the Debye temperature, one can show that

$$S_v = k_B \sum_i \ln\left(\frac{k_B T}{\hbar \nu_i}\right) = [\text{for perfect crystal}] = 3Nk_B \ln\left(\frac{k_B T}{\hbar \nu}\right)$$

In a crystal with $n$ vacancies:

$n \times z$ atoms have modified frequency $\nu'$

$N-n \times z$ atoms have the unperturbed frequency $\nu$

$z$ - coordination number

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Vibrational entropy of vacancy formation $\Delta s_v$

$$S_v = k_B \sum_i \ln \left( \frac{k_B T}{\hbar \nu_i} \right)$$

In a perfect crystal: $S_v^0 = 3Nk_B \ln \left( \frac{k_B T}{\hbar} \right)$

In a crystal with $n$ vacancies:

$n \times z$ atoms have modified frequency $\nu'$ and $N-n \times z$ atoms have the unperturbed frequency $\nu$

$$S_v^n = (3N - nz)k_B \ln \left( \frac{k_B T}{\hbar \nu} \right) + nzk_B \ln \left( \frac{k_B T}{\hbar \nu'} \right)$$

$$\Delta S_v^n = S_v^n - S_v^0 = nzk_B \ln \left( \frac{\nu'}{\nu} \right) = nk_B \ln \left( \frac{\nu}{\nu'} \right)^z$$

per vacancy: $\Delta s_v = \Delta S_v^i = k_B \ln \left( \frac{\nu}{\nu'} \right)^z$

for vacancies, $\nu' < \nu \implies \Delta s_v > 0$ generation of vacancy - interstitial pairs (Frenkel defects) can result in partial cancellation of $\Delta s_v$

for interstitials, $\nu' > \nu \implies \Delta s_v < 0$
Equilibrium vacancy concentration

\[
\frac{n_{eq}}{N} = \exp\left(\frac{\Delta s_v}{k_B}\right) \exp\left(-\frac{\Delta h_f}{k_B T}\right)
\]

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<td>(\Delta s_v/k_B)</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td></td>
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<td>1687</td>
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\(\Delta h_f \sim 1\) eV
\(\Delta s_v / k_B \sim 1 - 3\)

- assuming \(\exp\left(\frac{\Delta s_v}{k_B}\right) = 1\)

from Allen & Thomas

\(^a\) Bracht et al., PRL 91, 245502, 2003
\(^b\) Dannefaer, Mascher, Kerr, PRL 56, 2195, 1986
Divacancies and vacancy aggregates

If two vacancies join together and form a divacancy, the total number of “broken bonds” decreases and the energy of the divacancy is smaller than the sum of the enthalpies of the individual vacancies by binding enthalpy $h_b^{2v}$ (aka binding energy):

$$\Delta h_f^{2v} = 2\Delta h_f - h_b^{2v}$$

$$n_{eq}^{2v} \propto \exp\left(-\frac{\Delta h_f^{2v}}{k_BT}\right) = \exp\left(-\frac{2\Delta h_f - h_b^{2v}}{k_BT}\right)$$

$$n_{eq}^{1v} = N \exp\left(\frac{\Delta s_v}{k_B}\right) \exp\left(-\frac{\Delta h_f}{k_BT}\right) \propto \exp\left(-\frac{\Delta h_f}{k_BT}\right)$$

$$\frac{n_{eq}^{1v}}{n_{eq}^{2v}} \propto \exp\left(\frac{\Delta h_f - h_b^{2v}}{k_BT}\right)$$

since $\Delta h_f > h_b^{2v}$ (e.g., $h_b^{2v} \approx 0.1-0.2$ eV for fcc metals) the fraction of single vacancies decreases as $T$ increases. but even at $T \approx T_m$, most of the vacancies are the individual ones: $n_{eq}^{1v} / N \approx 10^{-4} - 10^{-3}$ and $n_{eq}^{2v} / N \approx 10^{-6} - 10^{-5}$ at $T \approx T_m$.

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Generation of vacancy aggregates upon quenching

Fast quenching can create a strong supersaturation vacancies - in the absence of nearby (within the diffusion length) sinks, the vacancies will meet each other and form divacancies, trivacancies, and larger clusters - this will reduce the enthalpy of the system.

Thus, in contrast to the equilibrium conditions, when the fraction of single vacancies increases as $T$ decreases, the fast cooling may decrease the fraction of single vacancies as the excess vacancies form divacancies and larger clusters.

The vacancy aggregates may grow into voids, prismatic dislocation loops or (for fcc metals) stacking fault tetrahedra.

TEM of stacking fault tetrahedra in quenched Au

Cottrell, *Phil. Mag.* 6, 1351, 1961
Sources and sinks of vacancies

\[
\frac{n_{eq}}{N} = \exp \left( \frac{\Delta s_v}{k_B} \right) \exp \left( - \frac{\Delta h_f}{k_B T} \right)
\]

Law of conservation does not apply to vacancies - they appear and disappear with temperature.

(1) free surfaces - original model by Frenkel (1945)
(2) grain and phase boundaries
(3) dislocations with an edge component
(4) 2D vacancy discs
(5) micro-pores

Different defects have different activation energies for vacancy formation but this does not affect the equilibrium vacancy concentration - from thermodynamics point of view, the process of vacancy formation is irrelevant. Equilibrium corresponds to reversible transfer of vacancies between the material and “vacancy vapor” or vacuum.

Elastic fields from various defects may affect the local equilibrium vacancy concentration - the equilibrium corresponds to the equity of chemical potentials at and in the vicinity of different crystal defects.
Time to equilibrium

for random distribution of sources/sinks, the relaxation time after sudden change of temperature:

\[ \tau \approx \frac{\langle L^2 \rangle}{AD_v} \]

\(<L^2>\) - mean squared vacancy diffusion path from/to the source/sink

\(D_v\) - vacancy diffusion coefficient

\(A\) - geometrical factor

quenching to \(T\) when \(D_v\) is sufficiently large for vacancies to reach each other, but not the sinks, local equilibrium may correspond to formation of vacancy clusters and pores

vacancy generation kinetics in polycrystalline gold samples quickly heated by electrical pulses from 436 to 653°C


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Methods of probing vacancy concentration

Experimental:
(1) Electrical resistivity
(2) Thermal conductivity
(3) Thermopower measurements
(3) Thermal expansion
(4) Heat capacity
(5) Positron-annihilation spectroscopy


Computational:
(1) Atomistic simulations with semi-empirical interatomic potentials
(2) Ab-initio (DFT-based) electronic structure calculations
Probing equilibrium vacancy concentration: Simmons & Balluffi, 1960

Simmons & Balluffi
Ag: Phys. Rev. 117, 600, 1960

generation of a vacancy = an extra lattice site in the crystal

measure change in bar length with camera:
\[
\frac{\Delta V}{V} = \frac{3\Delta L}{L} = \frac{n_v}{N} + \frac{\Delta V}{V}_{\text{th.ex.}} + \frac{\Delta V}{V}_{\text{relaxation}}
\]

measure change in lattice constant with XRD:
\[
\frac{\Delta a}{a} = \frac{1}{3} \left( \frac{\Delta V}{V} \right)_{\text{th.ex.}} + \frac{\Delta V}{V}_{\text{relaxation}}
\]

average dilatation due to the vacancies
Probing equilibrium vacancy concentration: Simmons & Balluffi, 1960

\[ \frac{3\Delta L}{L} = \frac{n_v}{N} + \frac{\Delta V}{V} \bigg|_{\text{th.ex.}} + \frac{\Delta V}{V} \bigg|_{\text{relaxation}} \]

\[ \frac{\Delta a}{a} = \frac{1}{3} \left( \frac{\Delta V}{V} \bigg|_{\text{th.ex.}} + \frac{\Delta V}{V} \bigg|_{\text{relaxation}} \right) \]

relaxation and thermal expansion effects cancel

\[ \frac{n_v}{N} = 3 \left( \frac{\Delta L}{L} - \frac{\Delta a}{a} \right) \]

determined from length-lattice parameter measurements

<table>
<thead>
<tr>
<th>material</th>
<th>( n_v/N ) at ( T_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>( 9.4 \times 10^{-4} )</td>
</tr>
<tr>
<td>Ag</td>
<td>( 1.7 \times 10^{-4} )</td>
</tr>
<tr>
<td>Au</td>
<td>( 7.2 \times 10^{-4} )</td>
</tr>
<tr>
<td>Cu</td>
<td>( 1.9 \times 10^{-4} )</td>
</tr>
<tr>
<td>Na</td>
<td>( 7.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>Pb</td>
<td>( 1.7 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

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Probing equilibrium vacancy concentration: Heat capacity

\[
\frac{n_{eq}}{N} = \exp\left(\frac{\Delta s_v}{k_B}\right) \exp\left(-\frac{\Delta h_f}{k_B T}\right)
\]

extra molar enthalpy due to the vacancies:

\[
\Delta H = n_{eq} \Delta h_f = \Delta h_f N_A \exp\left(\frac{\Delta s_v}{k_B}\right) \exp\left(-\frac{\Delta h_f}{k_B T}\right)
\]

\[
\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p = N_A k_B \left(\frac{\Delta h_f}{k_B T}\right)^2 \exp\left(\frac{\Delta s_v}{k_B}\right) \exp\left(-\frac{\Delta h_f}{k_B T}\right)
\]

difficult to separate the increase in the specific heat due to anharmonicity of interatomic interactions from the contribution of point defects
Atomistic simulation of vacancies

Atomistic simulations with semi-empirical interatomic potentials

Pair potentials:

The total potential energy of the system of $N$ atoms is

$$U(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) = \sum_{i} \sum_{j>i} U_2(\mathbf{r}_{ij})$$

where $\mathbf{r}_{ij} = |\bar{r}_j - \bar{r}_i|$.

Examples of commonly used pair potentials:

**Hard/soft spheres** – the simplest potential without any cohesive interaction

$$U_2(\mathbf{r}_{ij}) = \begin{cases} \infty & \text{for } \mathbf{r}_{ij} \leq r_0 \\ 0 & \text{for } \mathbf{r}_{ij} > r_0 \end{cases} \quad \text{- hard}$$

$$U_2(\mathbf{r}_{ij}) = \left(\frac{\mathbf{r}_{ij}}{r_0}\right)^{-n} \quad \text{- soft}$$

**Lennard-Jones** – van der Waals interaction in inert gases and molecular systems

$$U_2(\mathbf{r}_{ij}) = 4\varepsilon \left[ \left(\frac{\sigma}{\mathbf{r}_{ij}}\right)^{12} - \left(\frac{\sigma}{\mathbf{r}_{ij}}\right)^{6} \right]$$

**Morse** – similar to but is a more “bonding-type” potential compared to Lennard-Jones [Morse, Phys. Rev. 34, 57, 1930]

$$U_2(\mathbf{r}_{ij}) = \varepsilon \left[e^{-2\alpha(\mathbf{r}_{ij}-r_0)} - 2e^{-\alpha(\mathbf{r}_{ij}-r_0)} \right]$$
Atomistic simulation of vacancies

Problems with pair potentials:

Pair potentials do not have environmental dependence (e.g. atom in the bulk is too similar to the atom on the surface or near a defect site). In reality, the strength of the “individual bonds” should decrease as the local environment becomes too crowded due to the Pauli’s principle, but pair potentials do not depend on the environment and cannot account for this decrease.

Pair potentials do not account for directional nature of the bond. Covalent contributions (d orbitals) of the transition metals can not be described. Pair potentials work better for metals in which cohesion is provided by s and p electrons.

Quantitative problems:

The vacancy formation energy is significantly overestimated by pair potentials ($\Delta h_f \approx E_c$ with pair potential, $\Delta h_f \approx 0.21E_c$ for Au, $\Delta h_f \approx 0.35E_c$).

The ratio between the cohesive energy and the melting temperature, $T_m$, is underestimated by as much as 2-3 times. Metals have some “extra cohesion” that is less effective than pair potential in keeping the system in the crystalline state.

Atomistic simulation of vacancies

Solution - to introduce environmental dependence through the concept of local density

**Embedded Atom Method (EAM)**

\[
E_{\text{tot}} = \sum_i E_i \quad E_i = F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} U_2(r_{ij}) \quad \rho_i = \sum_{j \neq i} f_j(r_{ij})
\]


EAM potential accounts for the dependence of the interatomic interactions on local atomic density and allows one to reproduce both \(\Delta h_f\) and \(E_c\)

Direct electronic-structure (quantum-mechanics-based) calculations of interatomic interaction can be performed in so-called **ab-initio** atomistic simulation - Schrödinger equation for electrons is solved within the Density Functional Theory for a given set of positions of nuclei. In this case there is no need to assume a particular \(U(r_i)\), it is calculated during the simulation.