Thermodynamics Models based on DFT data for Hydrogen Supersaturation and Defects Stabilization

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Outline

1. The basic ingredients
   • Density Functional Theory
   • Statistic Thermodynamics (Gibbs free energy)

2. Thermodynamic models for vacancies

3. Supersaturation and vacancy stabilization

4. Discussion
1. The Basic Ingredient

**Density Functional Theory** – *electronic energy*

Calculating the **electronic energy** of a system of electrons and nuclei

- Should be done using *Quantum Mechanics*
- Achieved through solving the *Schrödinger equation*
- Solutions not known, approximation, Hartree-Fock
- **Limitation:** the wave-function depends on too many variables
  \[ \Psi(r_1, r_2, ..., r_N) \]
  for a system of N electrons

An alternative: the **Density Functional Theory**

- The **electronic density** \( \rho(r) \) only depends on three space variables
- The idea is to compute \( E[\rho] \)
- The question is how?
1. The Basic Ingredient

Density Functional Theory – *total energy*


Classical terms

Quantum terms:

- \( E^{\text{kin}}[\rho] \) – Known for non-interacting electrons
- \( E^{\text{exchange–correlation}}[\rho] \) – approximation

\( E^{\text{exchange–correlation}} \) – eXchange-Correlation functional

Total energy:

\[ E^{\text{DFT}} = E^{\text{elec}}[\rho] + E_{\text{nuclei–nuclei}} \]

Ground state energy

Does not include the Temperature
1. The Basic Ingredient

Density Functional Theory – vibrational frequencies

At $T = 0\text{K}$, only $v=0$ is populated.
Then, energy levels $v$ populated with increasing temperature.

Bulk system of $N$ atoms

3N – 3 frequencies $v_j$ (phonons)
Energy levels are populated with increasing temperature
Vibrational energy depending on the temperature

The energy of the system is made temperature dependent

$$E_{\text{tot}}(T) = E_{\text{DFT}}(0\text{K}) + E_{\text{vib}}(T)$$
1. The basic ingredients

- Density Functional Theory
- Statistic Thermodynamics

2. Thermodynamic models for vacancies creation

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1. The Basic Ingredient

Statistick Thermodynamics – *State function Energy*

Large number of particles \( \sim 10^{23} \)

\[
E_{\text{tot}}(T) = E_{\text{DFT}}(0K) + E_{\text{vib}}(T) + E_{\text{elec}}(T) + E_{\text{trans}}(T) + E_{\text{rot}}(T) + \ldots
\]

Bulk materials

Gas Phase

Two levels

\[
E_{\text{mean}}(T) = p_1(T) E_1 + p_2(T) E_2
\]

\( p_1(T) \) Boltzmann statistic

\[
E_{\text{mean}}(T) = \sum_j p_j(T) E_j
\]

\[
E_{\text{vib}}(T, \nu_j) = \sum_{j=1}^{n_{\text{vib}}} \hbar \nu_j \left( \frac{1}{2} + \frac{1}{\exp \left( \frac{\hbar \nu_j}{k_B T} \right) - 1} \right)
\]

\[
E_{\text{tot}}(T) = E_{\text{DFT}}(0K) + E_{\text{vib}}(T)
\]
1. The Basic Ingredient

**Statistic Thermodynamics**  – *Towards equilibria*

**Criterion for stability?**

\[ p_1(T) > p_2(T) \]

\[ p_2(T) \quad E_2 \]

\[ p_1(T) \quad E_1 \]

*Is E the criterion for stability?*

Because of the degeneracy, \( E_2 \) might be most populated depending on \( T \)

**Entropy**

\[ S(T) = -k_B \sum_j p_j(T) \ln p_j(T) \]
1. The Basic Ingredient

**Statistic Thermodynamics** – *State function Entropy*

\[ S(T) = -k_B \sum_j p_j(T) \ln p_j(T) \]

**Vibrational entropy**

\[ S^{\text{vib}}(T, \nu_j) = k_B \sum_{j=1}^{n^{\text{vib}}} \left[ \frac{\hbar \nu_j}{k_B T} \exp \left( \frac{\hbar \nu_j}{k_B T} \right) - 1 \ln \left( 1 - \exp \left( -\frac{\hbar \nu_j}{k_B T} \right) \right) \right] \]

**Configurational entropy**

Creating vacancies

\[ N \text{ lattice sites} \]
\[ N_{\text{at}} \text{ atoms at lattice sites} \]
\[ n_V \text{ vacancies at lattice sites} \]
\[ N = N_{\text{at}} + n_V \]

Number of configuration

\[ \Omega = \frac{(N_{\text{at}} + n_V)!}{N_{\text{at}}! \cdot n_V!} \]

**Entropy** (Boltzmann definition)

\[ S(T) = k_B \ln \Omega \]
1. The Basic Ingredient

**Statistic Thermodynamics** – *Equilibrium conditions*

**Helmoltz Free Energy**

\[ F(T) = E(T) - T \cdot S(T) \]

**Gibbs Free Energy**

\[ G(T) = H(T) - T \cdot S(T) \]

**Bulk:** \( F(T) \approx G(T) \)

**Potential**

Combines criterion on **energy** and **entropy**

**Conditions for equilibrium** - system of \( N \) components

**Gibbs free energy per particle for each \( j \) sub-system**

\[ g_j = e_j - T \cdot s_j \quad e_j(T) = e_j^{\text{DFT}} + e_j^{\text{vib}}(T) \quad s_j(T) = s_j^{\text{vib}}(T) \]

\[ G(T, p, n_1, n_2, ..., n_N) = \sum_j n_j \cdot g_j(T) - T \cdot S^{\text{conf}}(T) \]

\( \mu_j \) chemical potential

**Minimization**

Provides \( n_1^{eq}, n_2^{eq}, ..., n_N^{eq} \)
1. The basic ingredients

2. Thermodynamic models for vacancies
   • The model
   • Results of the model
   • Chemical potential and flux

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4. Discussion
2. Thermodynamics model for Vacancies

Perfect

\[ \text{Molecule } \text{H}_2 \]

\[ \text{Interstitial } \text{H}_i \]

\[ \text{Vacancy } \text{V} \]

Defects

\[ \text{VH}_j \text{ with } j = 0 - 12 \]

Electronic structure DFT calculations

\[ e_{\text{H}_2}^{\text{DFT}} \]

\[ e_{\text{H}_i}^{\text{DFT}} \]

\[ e_{\text{V}}^{\text{DFT}} \]

\[ e_{\text{VH}_j}^{\text{DFT}} \]

Vibrational frequencies DFT calculations

\[ \nu_{\text{H}_2} \]

\[ \sum_{k=1}^{3} \nu_k \]

\[ \sum_{k=1}^{3j} \nu_k \]
2. Thermodynamics model for Vacancies

Perfect

\[ g_j = e_j - T.s_j \]

\[ G(T,p,n_{H_2},n_{H_{1}},n_V,n_{VH_1},...n_{VH_{12}}) = \sum_j n_j \cdot g_j(T) - T \cdot S^{conf}(T) \]

Defects

\[ g_{H_2} = g_{H_2}^0 + k_B T \ln \frac{P}{P_0} \]

\[ g_{H_2}^0 = (e_{H_2}^{\text{rot}} + e_{H_2}^{\text{vib}} + e_{H_2}^{\text{trans}} + PV) - T(s_{H_2}^{\text{vib}} + s_{H_2}^{\text{rot}} + s_{H_2}^{\text{trans}}) \]


The minimizing against

\[ n_{H_2}, n_{H_{1}}, n_V, n_{VH_1},...n_{VH_{12}} \]
2. Thermodynamics model for Vacancies

Composition of the system at equilibrium

Reservoir $\mu$

$$G = \frac{1}{2} \left( \sum_{j=0}^{12} n_j \mu_{H_2} + n_{int} g_{int} + \left( \sum_{j=0}^{12} j n_j g_j \right) - T S_{conf} \right)$$

Minimization

x$_{H_i}$ (T) $\approx$ $\gamma$ exp $\left[ - \frac{g_{H_i} - \mu}{k_B T} \right]$  
H at interstitial

x$_{VH_j}$ (T) $\approx$ $\omega_j$ exp $\left[ - \frac{g_{VH_j} - j \mu}{k_B T} \right]$  
H in VH$_j$ vacancies

$$\mu = \frac{1}{2} g_{H_2} = \frac{1}{2} \left( g_{H_2}^° + k_B T \ln \frac{P}{P^°} \right)$$  
Chemical potential H$_2$ ideal gas

The chemical potential defines
- The fraction of H interstitial
- The fraction of VH$_j$ vacancies

Reversely H$_{int}$ defines
- The the chemical potential
- The fraction of VH$_j$ vacancies

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Formation of vacancies induced by interstitial H atoms


Interstitial H atoms impose a high chemical potential
This induces a high fraction of VHj vacancies

High temperature entropy favors interstitials
→ Vacancies are depopulated
2. Thermodynamics model for Vacancies

Driving forces for the formation of Super Abundant Vacancies

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</table>

SAV in Pd under High pressure
Y. Fukai and N. Okuma, PRL 73 (1994) 1640

Formation energy of VH$_j$ is lower than empty V up to j=6

E. A Hodille et al. PRMat 2 (2018) 093802
2. Thermodynamics model for Vacancies

Pioneering works on Mg and Al - Ismer et al. PRB 80 (2009) 184110

Ismer et al. PRB 80 (2009) 184110


$$H^i V H_j \text{ Reservoir } \mu$$

Dotted lines $x_{H_i}$
Bold lines $x_{H_{tot}} = x_{H_i} + \sum_{j=0}^{12} j \cdot x_{V H_j}$
2. Thermodynamics model for Vacancies

VHj formation in W


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Chemical potential fixed by the flux in the sub-surface


**Steady state**

 Flux balance

Experimental conditions

TRIM - depends on $E_{ion}$

DFT

$\chi_{Hi}^\text{MAX}_{t\to\infty} = R_p \cdot (1 - r) \cdot \frac{\phi_{ion}}{\rho W} \cdot \frac{1}{D(T)}$

$\phi_{surf}(t) \quad \phi_{bulk}(t)$

Surface

Bulk

Implantation depth

Migration depth

$R_p$

$R_d(t)$

$X_{Hi}$

$X_{Hi}^{\text{max}}(t)$

$(1 - r) \cdot \phi_{ion}$

H Supersaturation & V Stabilization, 11-12 April 2022
2. Thermodynamics model for Vacancies

Chemical potential fixed by the flux in the sub-surface


Atomic fraction of VHj vacancies in the 10 nm the sub-surface

The flux fixes $H_{int}$ …
- $H_{int}$ fixes the chemical potential…
- … and the fraction of $VH_j$ vacancies

$$x_{Hi} = R_p \cdot (1 - r) \cdot \frac{\phi_{ion}}{\rho_W} \cdot \frac{1}{D(T)}$$

$$x_{Hi} (T) \approx \gamma \exp \left[ - \frac{g_{Hi} - \mu}{k_B T} \right]$$

$$x_{VH_j} (T) \approx \omega_j \exp \left[ - \frac{g_{VH_j} - j \mu}{k_B T} \right]$$

Vacancy depopulation with increasing temperature

Incident flux $\phi_{inc} = 10^{19} \text{m}^{-2}\text{s}^{-1}$
Incident ion energy $E_{inc} = 500 \text{eV/ion}$.
2. Thermodynamics model for Vacancies

Chemical potential fixed by the flux in the sub-surface

**Flux**

\[ x_{H_i} = R_p \cdot (1 - r) \cdot \frac{\phi_{ion}}{\rho_W} \cdot \frac{1}{D(T)} \]

**H/D**

\[ \mu \]

**Response of the sub-surface**

\[ x_{H_i}(T) \approx \gamma \exp \left[ - \frac{g_{H_i} - \mu}{k_B T} \right] \]

\[ x_{VH_j}(T) \approx \omega_j \exp \left[ - \frac{g_{VH_j} - j \mu}{k_B T} \right] \]

**Incident fluxes** ranging from \( \phi_{inc} = 10^{17} \text{m}^{-2}\text{s}^{-1} \) to \( \phi_{inc} = 10^{24} \text{m}^{-2}\text{s}^{-1} \)

**Incident energy** of \( E_{inc} = 500 \text{ eV/ion} \).

The fraction of hydrogen **interstitial** sites is plotted in dotted lines.
3 – Super-Abundant Vacancies

Gao et al., Nucl. Fus. 57 (2017) 016026

Flux → W sample

\[ x_{H_i}(T) \quad \text{Perfect W} \]

\[ \mu \]

\[ x_{VH_j}(T) \quad \text{Defective W} \]

Surface

Phase Diagram

Incident flux \( [\text{m}^{-2}\text{s}^{-1}] \)

Temperature (K)

Temp. / Flux

No Impact of \( E_i \)

Nishijima et al. NF 61 (2021) 116028

No SSL – S. Kapser et al., NF (2018)

SSL – A. Manhard et al., NME (2018)

SSL – S. Kapser et al., NF (2018)

SSL - Gao et al., NF (2017)

SSL - Alimov et al., JNM (2005)

\[ E_{\text{inc}} = 70 \text{ eV} \]

\[ E_{\text{inc}} = 500 \text{ eV} \]
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1. The basic ingredients

2. Thermodynamic models for vacancies

3. Supersaturation and vacancy stabilization
   • Super Saturated Layers
   • Vacancy Stabilization

4. Discussion
3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

SSL forms within 10 nm

215 eV/D+ or 415 eV/H+

5eV/W at., well below 9eV/W at. (displ. Thr.)

Mechanisms for vacancy stabilization?

Hydrogen stabilizes vacancies

L. Gao et al. NF 57 (2017) 016026

E. A Hodille et al. PRMat 2 (2018) 093802
3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

SSL forms within 10 nm

- 215 eV/D+ or 415 eV/H+
- 5eV/W at., well below 9eV/W at. (displ. Thr.)

Mechanisms for vacancy stabilization?

- Hydrogen stabilizes vacancies
- Crowdion-SIA (and others) stabilizes vacancies
- Prevent them from recombining

E_f(VH\textsubscript{6}+SIA) = 12.1 eV
0.6 eV smaller than E_f(VH\textsubscript{6}) + E_f(SIA)

Kato et al. NF 55 (2015) 083019

L. Gao et al. NF 57 (2017) 016026
3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

SSL forms within 10 nm

215 eV/D+ or 415 eV/H+
5eV/W at., well below 9eV/W at. (displ. Thr.)

Mechanisms for vacancy stabilization?

*Binding energy of vacancies increases when vacancies grow*

*Crowdion-SIA (and others) stabilizes vacancies*

*Hydrogen stabilizes vacancies*

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L. Gao et al. NF 57 (2017) 016026

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3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

SSL forms within 10 nm

215 eV/D+ or 415 eV/H+
5eV/W at., well below 9eV/W at. (displ. Thr.)

More energy is required to dissociate the Frenkel pair in the absence of Hydrogen

Mechanisms for vacancy stabilization ?

Dynamic of the process ?
1. The basic ingredients

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SAV formation in damaged W – Defect Stabilization

M. Markelj et al., 59 (2019) 086050

4h W irradiation followed by 39 h D ions implantation

4h simult. W irradiation + D implantation followed by 35 h D ions implantation
3. Super-Saturation and Vacancy Stabilization

SAV formation in damaged W – Defect Stabilization

M. Markelj et al., 59 (2019) 086050

No help from the Thermo. Model

- SSL are formed in the near surface
- Vacancies annihilate with increasing T → higher mobility of the atom
- Decoration reveals the V remaining after damaging

4h W irradiation followed by 39 h D ions implantation
3. Super-Saturation and Vacancy Stabilization

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M. Markelj et al., 59 (2019) 086050

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M. Markelj et al., 59 (2019) 086050

\[ g_V + 6g_H \]

\[ g_{\text{VH}_6} + 6g_V \]

Temperature

Gibbs free energy, g

VH$_6$

Interstitial H

Toward VH$_6$ eq. during D imp. + W damage

Fluence not enough for reaching eq.  
→ The near surface is more populated

After W damage, created V not filled are reveal

With temperature, mechanism for V stab less and less efficient

4h simult. W irradiation + D implantation followed by 35 h D ions implantation
3. Super-Saturation and Vacancy Stabilization

SAV formation in damaged W – Defect Stabilization

M. Simmonds et al., 59 (2019) 086050

Complies with the Thermo model

To be discussed …
1. The basic ingredients

2. Thermodynamic models for vacancies

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4. Discussion
4. Discussion

- Mechanisms for SSL formation and V stab are probably the same
- H in V would stabilize a V and prevent it to recombines with SIA
- Thermal V are created at the surface. W atoms bring enough energy to create additional vacancies that would be stabilized with H. No need for collision cascade and Frankel pairs.
- The stress around VHj should be at shorter distance than around V. In addition, VHj is much less mobile the V. The cross section for VHj+SIA recombination is smaller than V + SIA.
- SSL are formed in other metals like Mo, Fe, steel, not Cu that display higher Ef for V creation
- Hy SSL are formed at T=800K. Is it because of the flux that bring µ so high?
Thanks for your attention …

… and sorry for being that long.