Vibrational contribution to the thermodynamics of nanosized precipitates: vacancy–copper clusters in bcc-Fe

Mina Talati¹, Matthias Posselt¹, Giovanni Bonny², Ahmed Al-Motasem¹ and Frank Bergner¹

¹ Helmholtz-Zentrum Dresden-Rossendorf (HZDR), PO Box 510119, D-01314 Dresden, Germany
² SCK-CEN, Boeretang 200, B-2400 Mol, Belgium

E-mail: mina.talati@gmail.com

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Abstract
The effects of lattice vibration on the thermodynamics of nanosized coherent clusters in bcc-Fe consisting of vacancies and/or copper are investigated within the harmonic approximation. A combination of on-lattice simulated annealing based on Metropolis Monte Carlo simulations and off-lattice relaxation by molecular dynamics is applied to obtain the most stable cluster configurations at $T = 0$ K. The most recent interatomic potential built within the framework of the embedded-atom method for the Fe–Cu system is used. The total free energy of pure bcc-Fe and fcc-Cu as well as the total formation free energy and the total binding free energy of the vacancy–copper clusters are determined for finite temperatures. Our results are compared with the available data from previous investigations performed using many-body interatomic potentials and first-principles methods. For further applications in rate theory and object kinetic Monte Carlo simulations, the vibrational effects evaluated in the present study are included in the previously developed analytical fitting formulae.

1. Introduction
The concentration of copper (0.03–0.3 wt%) in reactor pressure vessel (RPV) steels of existing fission reactors is typically higher than the solid solubility of Cu in Fe at RPV operational temperatures [1–3]. Neutron irradiation gives rise to a steady-state vacancy concentration that is orders of magnitude higher than in thermal equilibrium and enables Cu to diffuse efficiently via a vacancy mechanism [4, 5]. As a consequence, Cu-rich clusters form and take up a number of vacancies. In fact, mixed Cu–vacancy clusters with non-monotonically varying fractions of Cu and vacancies were observed recently in binary Fe–Cu alloys [6–8]. Similar processes take place in RPV steels, although other impurity and alloying elements may also play a role and vacancies seem to contribute less. Cu-rich clusters or precipitates in both binary Fe–Cu alloys (Cu content < 0.3 wt%) and RPV steels are typically smaller than 4 nm in diameter [8–10]. Experimental investigations [11, 12] also show that these Cu-rich precipitates are coherent, i.e. they possess the bcc structure of iron.

Irradiation-enhanced formation and evolution of the Cu-rich nanoclusters or precipitates are multiscale processes. These processes involve various physical phenomena and can be efficiently investigated with rate theory [5, 13] and object kinetic Monte Carlo (OKMC) simulations [14, 15] covering more or less realistic time and length scales. Important thermodynamic parameters, in particular the binding free energy of monomers (Cu atoms or vacancies) to defect clusters required for these coarse-grained or continuum approaches are, however, hardly accessible from experiments.
But atomistic computer simulations can provide these parameters.

In this study, our main objective is to quantitatively determine the vibrational contribution to the thermodynamics of defect clusters consisting of vacancies and/or Cu atoms in the Fe–Cu system with cluster sizes larger than first-principles methods can treat. For this purpose, the most recent interatomic potential for the Fe–Cu alloy is employed [16]. We perform here a combination of Metropolis Monte Carlo (MMC) simulations and molecular dynamics (MD) simulations to find the energetically most stable defect configurations. This method was previously employed by Al-Motasem et al [17] and is similar to the procedures used by Takahashi et al [18] and Kulikov et al [19]. To determine the vibrational effects, we find the phonon frequencies of the stable structures under the harmonic approximation, with the computation of thermodynamic quantities following the total formation free energy and the total binding free energy for pure and mixed defect clusters are calculated. Moreover, in order to furnish the input parameters for further applications in rate theory and OKMC simulation, we also aim here to provide simple but practicable analytical fitting formulae that render the total and the monomer binding free energy of defect clusters for finite temperatures. The computational procedure is detailed in section 2. Results are presented and discussed in section 3, followed by the summary and conclusion of this work.

2. Computational method

In order to find the most stable configurations of coherent clusters consisting of \( l \) vacancies and \( m \) Cu atoms (i.e. \( v_l\text{Cu}_m \) clusters), at first we performed on-lattice simulated annealing based on Metropolis Monte Carlo (MMC) simulation as described in [17]. The initial configurations contained randomly distributed isolated vacancies and Cu atoms at 600 K. Then we decreased the temperature to 0 K, reducing it by 60 K every 100 MMC steps. A single cluster is found at 0 K for all cases considered in this study. Subsequently we performed a quasi-dynamic quench through molecular dynamics simulation at 0 K to relax the positions of Fe and Cu atoms off-lattice following the procedure reported in [17]. The lowest formation energy, \( E_l(v_l\text{Cu}_m) \), is then obtained by performing several such relaxations for slightly different values of the lattice constant. This quantity is defined as

\[
E_l(v_l\text{Cu}_m) = E(v_l\text{Cu}_m) - (N - l - m)E_{\text{Fe}}^{\text{coh}} - mE_{\text{Cu}}^{\text{coh}}.
\]

where \( N \) is the total number of regular lattice sites. \( E(v_l\text{Cu}_m) \) is the configurational energy of the simulation box containing the most stable configurations of the \( v_l\text{Cu}_m \) cluster. \( E_{\text{Fe}}^{\text{coh}} \) and \( E_{\text{Cu}}^{\text{coh}} \) represent the cohesive energy per atom of bcc-Fe and fcc-Cu, respectively (\( E_{\text{Fe}}^{\text{coh}} = -4.122 \) eV and \( E_{\text{Cu}}^{\text{coh}} = -3.540 \) eV for chosen interatomic potential) which are chosen as reference systems. The total binding energy of a \( v_l\text{Cu}_m \) cluster, \( E_{\text{bind}}(v_l\text{Cu}_m) \), describes the energy change when isolated vacancies and Cu atoms are combined to form a cluster and is defined by

\[
E_{\text{bind}}(v_l\text{Cu}_m) = E_l(v_l\text{Cu}_m) - lE_l(v_1) - mE_l(\text{Cu}_1),
\]

where \( E_l(v_1) \) and \( E_l(\text{Cu}_1) \) are the formation energy of a monovacancy and of a single Cu atom, respectively (cf equation (1)). \( E_l(\text{Cu}_1) \) is also called substitutional energy. Negative values of \( E_{\text{bind}}(v_l\text{Cu}_m) \) suggest an energetically favourable condition for the monomers to form a cluster. We employed here the most recent and currently the most suitable many-body interatomic potential of Pasianot and Malerba (PM) [16] developed for the description of radiation effects in Fe–Cu binary alloys. It is based on the Mendelev [21] and the Mishin [22] potentials for pure Fe and Cu, respectively. The simulation box of bcc-Fe lattice is chosen to be cubic in shape with each edge of 10\( a \) in length, where \( a \) is the lattice constant. Three-dimensional periodic boundary conditions are applied. In this study, pure clusters containing up to 80 either vacancies or copper atoms are considered. Maximum cluster size amounts to a total of 100 vacancies and copper atoms for mixed clusters. In agreement with experimental findings [11, 12] all the clusters considered in this paper are assumed to possess the bcc structure of iron.

In this work the vibrational contribution to the thermodynamics of cluster configurations which are the most stable at \( T = 0 \) is considered. However, it should be noted that at finite temperatures the (spatial) cluster configuration with the lowest free energy may differ from the most stable configuration at \( T = 0 \). In general, one has to determine both vibrational and configurational contributions to the thermodynamics of the clusters in order to find a cluster with the lowest free energy at finite temperature. The still unresolved puzzle of vibrational and configurational contributions to the free energy of embedded clusters of given size and composition is beyond the scope of the present work but is a subject of ongoing investigation.

Under the harmonic approximation, at the \( \Gamma \)-point the phonon frequencies \( \alpha_i \) are determined by diagonalizing the dynamical matrix \( \Phi_{ij} \) defined as

\[
\Phi_{ij} = -\left( \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 F_i}{\partial r_j^2} \right),
\]

where \( m_i \) is the mass of the \( i \)th atom. It is calculated by applying small displacements \( r_j \) away from their most stable atomic positions and evaluating the subsequent induced forces \( F_i \) and force derivatives \( \partial F_i / \partial r_j \).

The phonon calculations allow us to compute various thermodynamic properties, e.g. free energy, entropy, heat capacity, etc. The vibrational contribution to the total free energy (from now on the vibrational free energy) of a solid, \( G_{\text{vib}} \) at finite temperature \( T \) is calculated using the following expression:

\[
G_{\text{vib}}(V, T) = \frac{U_{\text{vib}}(V, T) - TS_{\text{vib}}(V, T)}{T},
\]

where \( U_{\text{vib}}(V, T) \) represents the vibrational internal energy and \( S_{\text{vib}}(V, T) \) the vibrational entropy. In the harmonic approximation these contributions (cf equations (5) and (6)) are represented as the sum of individual normal frequencies, \( \alpha_i \). The total number of individual normal frequencies are three times the total number of atoms in the primitive cells. Because of the translational invariance of the system three
The phonon density of states gives the number of vibrational modes per phonon frequency. Vanishing bin size, gives the number of vibrational modes per phonon frequency. An alternative way to calculate the vibrational free energy ($G_{vib}^{\text{total}}$) here is through the phonon density of states (PDOS), $g(\omega)$:

$$G_{vib}^{\text{total}}(V, T) = (3N - 3) \int_0^\infty k_B T \ln \left( 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \right) \times g(\omega) \, d\omega,$$

where $g(\omega)$ is normalized so that

$$\int_0^\infty g(\omega) \, d\omega = 1. \tag{8}$$

The phonon density of states $g(\omega)$, which can also be considered as a histogram of phonon frequencies with vanishing bin size, gives the number of vibrational modes per phonon frequency.

The vibrational part of the total formation free energy of a $\nu_l \text{Cu}_{m}$ cluster configuration, the most stable at $T = 0$, is calculated from the following expression:

$$G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T) = G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T)
- (N - l - m)G_{\text{coh}}^{\text{vib}}(\text{Fe}, V, T) - mG_{\text{coh}}^{\text{vib}}(\text{Cu}, V, T), \tag{9}$$

where $G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T)$ determined using equation (7) represents the vibrational free energy of the system with the $\nu_l \text{Cu}_{m}$ cluster. $G_{\text{coh}}^{\text{vib}}(\text{Fe}, V, T)$ and $G_{\text{coh}}^{\text{vib}}(\text{Cu}, V, T)$ represent the vibrational contribution to the cohesive energy per atom at given temperature ($T$) and volume ($V$) of bcc-Fe and fcc-Cu, respectively. The total formation free energy is then written as

$$G_{l}^{\text{Total}}(\nu_l \text{Cu}_{m}, V, T) = E_{l}(\nu_l \text{Cu}_{m}) - T S_{l}^{\text{conf}}(\nu_l \text{Cu}_{m})
+ G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T), \tag{10}$$

where $S_{l}^{\text{conf}} (= k_B \ln W)$ is the formation entropy at $T = 0$ K which is determined by the number $W$ of different three-dimensional arrangements of a cluster with a given shape at a given position. In the present paper the contribution of $S_{l}^{\text{conf}}(\nu_l \text{Cu}_{m})$ is neglected. Its determination is a subject of ongoing investigation.

The vibrational part of the total binding free energy and the total binding free energy can be obtained in a similar fashion from the following formulae:

$$G_{\text{bind}}^{\nu_l \text{Cu}_{m}, V, T} = G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T)
- mG_{l}^{\text{vib}}(\text{Cu}_1, V, T), \tag{11}$$

and

$$G_{l}^{\text{Total}}(\nu_l \text{Cu}_{m}, V, T) = E_{l}(\nu_l \text{Cu}_{m}) + G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T) \tag{12}$$

where $G_{l}^{\text{vib}}(\nu_l \text{Cu}_{m}, V, T)$, $G_{l}^{\text{vib}}(\nu_l, V, T)$ and $G_{l}^{\text{vib}}(\text{Cu}_1, V, T)$ represent the vibrational part of the total formation free energy of the $\nu_l \text{Cu}_{m}$ cluster, of a monovacancy and a single Cu in bcc-Fe, respectively (cf equation (9)). $E_{\text{bind}}(\nu_l \text{Cu}_{m})$ represents the binding energy of a cluster at 0 K (cf equation (2)).

The monomer binding free energy is the binding energy of a monovacancy or of a single Cu atom to a pure $\nu_l$ or $\text{Cu}_{m}$ cluster. This quantity, at $T \neq 0$ and zero pressure, is required as input parameters for rate theory and object kinetic Monte Carlo simulations and can be determined from the following expression:

$$G_{l}^{\text{Total}}(\nu_l, V, V, T) = G_{l}^{\text{Total}}(\nu_l, V, T) - G_{\text{bind}}^{\nu_l}(V_{l-1}, V, T) \tag{13}$$

Figure 1 depicts the phonon density of states (PDOS) of pure bcc-Fe and fcc-Cu, which are in good agreement with the available experimental observation and theoretical calculations [23–26]. The PM potential which is based on the Mendeleev potential [21] for pure Fe and on the Mishin potential [22] for pure Cu seems to reproduce the experimental phonon density of states of elemental bcc-Fe and fcc-Cu well. The vibrational free energy of the considered systems is then calculated using their PDOS in equation (7). As shown in figure 2 our results for bcc-Fe and fcc-Cu are compared with the Scientific Group Thermodata Europe (SGTE) database and results from other interatomic potentials for these two elements [27–31]. The methodology to produce this database includes CALPHAD calculations and experimental data and it provides the thermodynamic data for inorganic and metallurgical systems. The calculations use empirical interpolation formulae and experimental input to describe the phase diagram of materials. The vibrational free energy of bcc-Fe and fcc-Cu calculated within the framework of the harmonic approximation fall very much into the range of available literature data. At 1200 K the calculated vibrational free energy of bcc-Fe using the PM potential is about 160 meV and 100 meV higher than the thermodynamic database [27] and the CALPHAD data [28], respectively. However, it falls within a 50 meV range of vibrational free energy calculated using other interatomic potentials such...
as the Meyer–Entel potential, the Johnson potential, which is a recent update of the Johnson–Oh potential, and the Finnis–Sinclair potential [29]. At around 600 K, close to the operating temperature of a nuclear reactor, the former difference in the vibrational free energy is about 70 meV and 30 meV, respectively, while the latter is within a 20 meV range. The Meyer–Entel potential predicts the highest values of the vibrational free energy and hence the furthest from the literature [27, 28] while the PM potential provides the closest values. Similarly, though the Ludwig–Farkas potential predicts the vibrational free energy of the fcc-Cu (in [30]) closest to the available database [27], the PM potential calculates it within the closer range of 30 meV and 10 meV at 1200 K and 600 K, respectively. The ability to reproduce the experimental PDOS of bcc-Fe and fcc-Cu to a satisfactory extent and to predict their vibrational free energy close to the SGTE database shows that the choice of the PM potential is justified for the considered systems in the present work.

3.2. Formation free energy of the clusters

For the defect clusters containing vacancies and substitutional Cu atoms in bcc-Fe considered in the present work, the peak positions in the PDOS of bcc-Fe and its form do not show any visible difference from one another. This indicates the very weak effect of the considered number of vacancies and substitutional Cu atoms in the defect clusters in bcc-Fe. For this reason, the PDOS of defect clusters in bcc-Fe are not shown here. A first-principles study for a monovacancy in bcc-Fe also reports a similar observation with a slight phonon spectrum shift towards lower frequencies [32].

Figure 3(a) depicts the total formation free energy of a monovacancy in bcc-Fe. In the present study using the PM potential the value for the formation energy of a monovacancy is \( E_f(v_1) = 1.710 \) eV [17]. This value is in satisfactory agreement with data obtained by positron annihilation spectroscopy ((1.60 ± 0.15) eV [34], 1.5 eV [35], (2.0 ± 0.2) eV [36] and 1.85 eV [37]) although lower than predicted by DFT calculations (2.11 eV [32], 2.15 eV [38], 1.95 eV [39], 2.02 eV [40], 2.17 eV [41] and 2.09 eV [42]). The vibrational contributions lower the total formation free energy \( G_{\text{Total}}(v_1, T) \) of the monovacancy at higher temperatures as shown in figure 3(a). Due to an increase in vibrational interactions (or thermal excitations) with temperature, the probability to form vacancies in a lattice also increases. Recent computational investigations on the vibrational contribution to the formation energy of the monovacancy
in bcc-Fe with both first-principles calculations [32] and
many-body interatomic potentials [33] also conform to our
results (cf figure 3(a)). Note that only in the calculation
of Mendeleev et al [33] were anharmonic effects taken into
account whereas the first-principles calculations [32] used
the harmonic approximation. Since in the present work and
in the paper of Mendeleev et al [33] the same interatomic
potential was employed, the stronger decrease of the data
of Mendeleev et al above 900 K seems to be related to
anharmonic effects. Nevertheless, in overall agreement with
the temperature dependence of our results with that of the
two datasets [33, 32] on the vibrational contribution to the formation free energy of a single Cu atom
in bcc-Fe. This has been considered in the present work
and the result is depicted in figure 3(b). In contrast to the
results for the monovacancy, the total formation free energy
of a single Cu atom slightly increases with temperature.
This leads to a decrease of the solubility of Cu in Fe
and worsens the agreement with the experimental data (see
figure 4). In order to check the influence of anharmonic
effects the vibrational contribution to the free formation
energy of a single Cu atom was determined by the method
of thermodynamic integration [45, 46] but again an increase
with temperature was obtained. Obviously, this effect is due
to the PM potential [16] used in our calculations. This result
should be taken into account in future applications of this
potential. Nevertheless we have used the PM potential to
determine the vibrational contributions to the free formation
energies of pure Cu clusters and mixed vacancy–copper
clusters containing up to 100 monomers. The results are
discussed below. Before, the only available literature data on
the vibrational contribution to the formation free energy of a
single Cu atom in bcc-Fe are discussed. They were obtained
from first-principles calculations [26] (see figure 3(b)) and
show a decrease with temperature, in contrast to our results.
Since first-principles calculations are generally considered to
be more accurate than those using interatomic potentials,
the slight increase with temperature found using the PM potential
seems to be an artefact. Also, the substitutional energy of Cu
provided by the PM potential \( E_f^{\text{Cu}} = 0.4369 \text{ eV} \) seems
to be too low compared to 0.77 eV from [26]. These authors
have also demonstrated that their data as shown in figure 3(b)
lead to reasonable values for the Cu solubility in Fe, at least at elevated temperatures above 900 K.

The total formation free energy of pure Cu clusters (Cuₘ) increases with temperature within a range of 2 eV over the considered temperature range as shown in figure 5(b). This increase in $G_{\text{f, total}}^{\text{Cuₘ}}(V,T)$ means that formation or substitution of Cu clusters in a bcc-Fe matrix becomes somewhat more difficult at elevated temperature. We assume that this unusual behaviour is again due to the PM potential [16] employed in our calculation. However, only first-principles investigations can finally clarify this issue.

Mixed vacancy–Cu clusters ($v_l$Cuₘ) as shown in figure 5(c) exhibit the effect of vibrational contribution (i.e. $G_{\text{f, vib}}^{\text{Cuₘ}}(v_l\text{Cuₘ}, V,T)$) by reducing the values of their total formation free energy with temperature. The similar effect is also observed in the case of pure vacancy clusters ($v_l$). Moreover, the number of vacancies present in $v_l$Cuₘ clusters seems to dominate the value of the formation energy of $v_l$Cuₘ clusters (i.e. $E_l(v_l\text{Cuₘ})$ and total formation free energy, $G_{\text{f, total}}^{\text{Cuₘ}}(v_l\text{Cuₘ}, V,T)$, in particular the temperature dependence of the latter quantity. The reduced values of $G_{\text{f, total}}^{\text{Cuₘ}}(v_l\text{Cuₘ}, V,T)$ at higher temperatures suggest the increased tendency of formation of mixed $v_l$Cuₘ clusters and such mixed clusters are easier to form compared to pure $v_l$ clusters (cf figures 5(a) and (c)). In fact, in all cases discussed above, $E_l(v_l\text{Cuₘ})$ primarily determines the values of $G_{\text{f, total}}^{\text{Cuₘ}}(v_l\text{Cuₘ}, V,T)$. The contribution from $G_{\text{f, vib}}^{\text{Cuₘ}}(v_l\text{Cuₘ}, V,T)$ determines the trend of $G_{\text{f, total}}^{\text{Cuₘ}}(v_l\text{Cuₘ}, V,T)$ with temperature.

3.3. Binding free energy of the clusters

Figure 6(a) shows that the absolute value of total free binding energy for pure $v_l$ clusters, $G_{\text{bind}}^{\text{Total}}(v_l, V,T)$, decreases with temperature. This decrease is associated with the increased vibrational contribution. The decreased absolute values of $G_{\text{bind}}^{\text{Total}}(v_l, V,T)$ indicate that the vibrational contribution weakens the bonding of pure $v_l$ clusters at elevated temperatures. In other words, pure vacancy clusters are less stable at elevated temperatures. At an operating temperature of a nuclear reactor close to 600 K, the absolute values of total binding free energy are about 6% smaller than their corresponding values at 0 K.

Pure Cuₘ clusters exhibit an increase in absolute values of $G_{\text{bind}}^{\text{Total}}(v_l\text{Cuₘ}, V,T)$ as shown in figure 6(b) with increasing temperature, which indicates that vibrational contributions strengthen the bonding of pure Cuₘ clusters at elevated temperatures. This increase also means that pure Cu clusters are more stable at higher temperatures. This behaviour should again be a consequence of the PM potential [16] employed in our calculation. The absolute values of total binding free energy at about 600 K are observed to increase by about 3–6% compared to $E_{\text{bind}}(v_l\text{Cuₘ})$ at 0 K. Surprisingly, the absolute values of total free binding energy of small Cuₜ₀ clusters at 800 K determined in this work show a good agreement with results of first-principles calculations reported at 773 K [20]. As already mentioned above, more first-principles studies are required to obtain fully convincing results on the precision of the data obtained in this work using the PM interatomic potential.

As shown in figure 6(c) the absolute values of $G_{\text{bind}}^{\text{Total}}(v_l\text{Cuₘ}, V,T)$ of all mixed vacancy–copper clusters considered here decrease with increasing temperature. At 1200 K the decrease ranges from $\sim$1 eV for $v_{10}$Cuₜ₀ clusters to $\sim$12 eV for $v_{90}$Cuₜ₀. The $v_{20}$Cuₘ, $v_{40}$Cuₘ and $v_{60}$Cuₘ clusters exhibit a decrease of $\sim$3–5 eV, $\sim$6–8 eV and $\sim$8–10 eV, respectively, at 1200 K, where $m = 20, 40$ and
the trend of the total binding free energy of pure

\( G \) (not shown here) and appears to follow

the trend of the total binding free energy of pure \( v_l \) clusters

with increase in temperature. In other words, the decrease

in the absolute values of total binding free energy as a

function of temperature indicates the higher probability of
dissociation of these mixed clusters into their constituents, i.e.

\( l \) monovacancies and \( m \) single Cu atoms. At about 600 K the

absolute values of total binding free energy of \( v_l Cu_m \) clusters

is observed to reduce by a minimum of \(~2.5\%\) for \( v_{10}Cu_{10} \)
to a maximum of about 6\% for \( v_{80}Cu_{20} \) in comparison with their

corresponding values at 0 K. The \( v_{20}Cu_m \), \( v_{40}Cu_m \) and

\( v_{60}Cu_m \) clusters show a reduction of \(~5–3\%\), \(~6–4\%\) and

\(~6–5\%\), respectively, at 600 K in the absolute values of their

\( G_{bind}^{Total} (v_l Cu_m, V, T) \) compared to their corresponding values

at 0 K.

In order to summarize the results of the atomistic

simulations performed in this work for further use in

rate theory and object kinetic Monte Carlo simulations

(cf section 1) a compact description of these data by analytical

formulas is desirable. Physically based relations between

cluster free energies and the cluster size can be found in

the literature (e.g. [49, 50]). In particular, for Cu clusters in Fe,
it was shown that a simple description including the powers 1

and 2/3 of the cluster size is sufficient and the power 1/3 and

the log dependences can be neglected [50]. This corresponds
to the so-called capillary model [5, 13] that was recently used

by Al-Motasem et al [17] to establish a simple fitting formula

for the dependence of total binding free energy at 0 K of pure

clusters on cluster size:

\[
E_{bind}(v_l) \approx a l^{2/3} + b l + c
\]

\[
E_{bind}(Cu_m) \approx d m^{2/3} + e m + f.
\]

These fits are valid for \( l, m \geq 2 \). The values of the

fitting parameters \( a (=2.805 95 \text{ eV}) \), \( c (=1.536 77 \text{ eV}) \),

\( d (=0.596 67 \text{ eV}) \) and \( f (=0.601 87 \text{ eV}) \) are determined by

setting \( b \) and \( e \) to the negative formation free energies at 0 K

of the corresponding monomers, i.e. \( b = -E_l(v_1) = -1.71 \text{ eV} \)

and \( e = -E_l(Cu_1) = -0.4369 \text{ eV} \).

The analytical relations in equation (15) are chosen in

such a way that the analytical form of their derivatives, i.e.

\[
E_b(v, v_l) \approx \frac{dE_{bind}(v_l)}{dl} = \frac{2}{3} a l^{-1/3} + b
\]

\[
E_b(Cu, Cu_m) \approx \frac{dE_{bind}(Cu_m)}{dm} = \frac{2}{3} d m^{-1/3} + e
\]

corresponds to the relation for the monomer binding free

energy used in conventional rate theory (cf equation (4)
in [5] for 0 K). The coefficients \( a \) and \( d \) are related to the

quantity \( \gamma V_{at}^{2/3} (36 \pi)^{1/3} \) given in [5], where \( \gamma \) denotes

the cluster–matrix interface energy and \( V_{at} \) the atomic volume in

the bcc-Fe.

The vibrational contributions to the total binding free

energy of the clusters determined in this work by atomistic

simulations are included using the dependence on cluster size

given in (15) and employing a purely phenomenological fit

for the temperature dependence of the pre-factors:

\[
G_{bind}^{Total}(v_l, V, T) \approx d'(T) l^{2/3} + b'(T) l + c'(T)
\]

\[
G_{bind}^{Total}(Cu_m, V, T) \approx d'(T) m^{2/3} + e'(T) m + f'(T)
\]

with

\[
d'(T) = 2.766 02 - 2.691 98 \times 10^{-4} T
\]

\[
b'(T) = -G_{bind}^{Total}(v_1, V, T)
\]

\[
= -1.709 68 + 1.704 04 \times 10^{-4} T
\]
\[ c'(T) = -1.189 \times 10^{4} + 1.074 \times 10^{5} T - 3.564 \times 10^{-8} T^2 \]
\[ d'(T) = 0.56749 - 3.8371 \times 10^{-5} T \]
\[ e'(T) = -G_{T=0}^{\text{total}}(\text{Cu}, V, T) = -0.4382 - 4.0428 \times 10^{-4} T \]
\[ f'(T) = -0.47811 + 1.82043 \times 10^{-4} T - 4.02524 \times 10^{-8} T^2. \]

The monomer binding free energy at \( T \neq 0 \) defined in equation (13) can then be determined by treating equation (17) with the similar analytical approximations introduced in equation (16).

It should be emphasized once more that the main purpose of the analytical formulae given above is to provide a sufficiently simple, compact and practicable summary of the data determined by the atomistic simulations. From the viewpoint of a strict nucleation theory these relations may therefore be considered as phenomenological.

4. Summary and conclusion

In this paper, we report our work on vibrational contributions to the thermodynamics of nanosized vacancy–copper clusters in bcc-iron. The most recent many-body interatomic potential developed by Pasianot and Malerba is employed. Vibrational effects are calculated under the harmonic approximation. We summarize our results as follows:

(i) The vibrational free energy of bcc-Fe and fcc-Cu compares well with the SGTE database and data from the other interatomic potentials.

(ii) With increasing temperature the vibrational contributions lead to a decrease of the total formation free energy of the monovacancy which is in agreement with the few data available from the literature. This result means an enhanced activity of vacancy formation in bcc-Fe at elevated temperatures.

(iii) The observed decrease of the total formation free energy and of the absolute values of the total binding free energy of pure vacancy clusters with increasing temperature indicates a higher probability of the dissociation into individual vacancies. The absolute values of the total binding free energy of pure vacancy clusters show a decrease of about 6% at the operating temperature of a nuclear reactor of about 600 K as compared to their values at 0 K.

(iv) Contrary to the case of the monovacancy, the total formation free energy of a single Cu atom increases with temperature. This leads to a decrease of the solubility of Cu in Fe and to a deterioration of the agreement with the corresponding experimental data compared to previous solubility calculations without including vibrational effects. This result is obviously due to the PM potential used in our calculations. It has to be taken into account in future applications of this potential. On the other hand, first-principles data from the literature show a decrease of the total formation free energy of a single Cu atom with increasing temperature. Despite this finding we have used the PM potential to determine the vibrational contributions to the free formation energies of pure Cu clusters and mixed vacancy–copper clusters containing up to 100 monomers.

(v) The thermodynamics of a single Cu atom in Fe obtained using the PM potential leads to an increase of the total formation free energy and of the absolute value of the total binding free energy of pure Cu clusters with increasing temperature. This suggests a lower probability of the dissociation of the pure Cu clusters into individual components at increased temperatures. The absolute values of the total binding free energy of pure Cu clusters show an increase of about 3–6% at about 600 K as compared to their corresponding values at 0 K.

(vi) Due to the dominating influence of vacancies on the thermodynamics of the mixed vacancy–copper clusters considered in this work, the corresponding values for formation free energy and total binding free energy show a temperature dependence similar to that of pure vacancy clusters. The absolute values of the total binding free energy of mixed clusters show a decrease from a minimum of ~2.5% to a maximum of ~6% at about 600 K as compared to their corresponding values at 0 K, depending on the number of vacancies present in the clusters.

(vii) Finally, the temperature dependence of the binding free energies obtained in this work is included in previously developed analytical fits in order to provide a sufficiently simple, compact and practicable summary of the calculated data for further use in rate theory and object kinetic Monte Carlo simulations.

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