



Atomistic study of the thermodynamic equilibrium of nano-sized helium cavities in β SiC

Adrien Couet^a, Jean-Paul Crocombette^{a,*}, Alain Chartier^b

^aCEA-Saclay, DEN/DMN/SRMP, 91191 Gif-sur-Yvette, France

^bCEA-Saclay, DEN/DPC/SCP, 91191 Gif-sur-Yvette, France

ARTICLE INFO

Article history:

Received 29 October 2009

Accepted 16 June 2010

ABSTRACT

The estimation of the number of inert gas atoms contained at equilibrium in microscale bubbles in a solid usually relies on a well-known formula equilibrating the internal pressure of He to the surface energy of the bubble. This approach evidences a strong variation with temperature of He content for a given bubble. At the opposite, at the Angstrom scale, ab initio calculations for He contained in vacancy assemblies neglect temperature effects. In this work, empirical potential molecular dynamics simulations are used to study, in the case of helium inserted in cubic silicon carbide, the variation of the He content of sub-nanoscale cavities with temperature. To do so free energy for He atoms inserted in cavities made of a few vacancies (up to 29) are calculated. One then evidences the existence of a sub-surface segregation in interstitial sites close to the surface of the cavity. The variation of the He content with temperature is observed to be negligible at the nanoscale, thus validating the ab initio approach.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Silicon carbide (SiC) is known to have a good resistance to neutron radiation damage [1,2] thanks to many desirable attributes for high-temperature applications in a neutron radiation environment such as high chemical and thermal stability, low activation and high strength. For these and other reasons, SiC based materials is considered for use in fusion energy systems as first wall or blanket materials. When SiC is submitted to a high flux of energetic neutrons (14 MeV in the first wall of fusion reactor), transmutation nuclear reactions and emergence of helium bubbles in SiC [1] are observed. Several past studies have been carried out to examine the behavior of He in SiC [2,3] and have permitted to understand a lot of properties of these helium bubbles. However few of them have precisely investigated the behavior of He gas in equilibrium bubbles at finite temperature. Notably, it is very important to know the number of helium atoms in an equilibrium bubble to determine such properties of SiC under irradiation as the release and retention behavior of helium in these bubbles.

Experimentally, the determination of the number of He atoms inside a bubble in a material usually rely on the well-known relationship [4,5] between the internal pressure of He in the bubble P and the surface energy of the cavity σ .

$$P = \frac{2\sigma}{R} \quad (1)$$

* Corresponding author.

E-mail address: jpcrocombette@cea.fr (J.-P. Crocombette).

for all radii R of bubbles which are assumed to be spherical. With this pressure equilibration formula the number of gas atoms that can be incorporated in a bubble hugely depends on temperature; basically it is proportional to the inverse of temperature in the limiting case of a perfect gas.

At the opposite, ab initio atomistic simulations can provide very accurate energetic predictions [6–8]. But due to huge simulation times, these simulations are restricted to extremely small cavities made of less than about five vacancies. Moreover for the same computational reasons, these calculations are restricted to zero temperature.

Our goal in this work is to study the effect of temperature on the number of He atoms in very small cavities. To do so we use empirical potential Molecular Dynamics (MD) in which we deal the quantitative accuracy of the ab initio calculation for the ability to consider finite temperature effects. We are then able to calculate the free energies of He atoms in the cavities and to compare them with the free energy of He in the bulk of silicon carbide. Our idea was to compare the free energies of He atoms inside the cavity to their free energy in the bulk. The sign of the difference between these two free energies indicates whether it is in a more favorable situation in the bulk or in the cavity. Starting from only one He in a cavity, we added one helium after the other in the cavity as long as their free energy remains lower than in the bulk. As soon as it would become larger one would have exceeded the number of helium atoms at equilibrium in the given cavity. This procedure assumed that all He atoms would remain inside the cavity. This assumption proved wrong which sheds light on the actual behavior of He atoms in and close to cavities.

We first describe the technicalities of this work and especially the empirical potentials used in the study. We then focus on the calculation of the free energy and spatial repartition of He atoms inserted in sub-nanoscale cavities.

2. Technicalities

2.1. Empirical potentials

SiC cohesion is described by a Tersoff–Brenner potential already used in previous works on SiC thermal properties [9–12]. He–He interactions are described by the well-known pair interaction designed by Tang and Toennies [13] with enough terms in the dispersion series to assure a good convergence of the Born–Mayer parameters. New He pair interactions with Si and C were derived from ab initio calculations on the insertion sites of He in SiC [15]. As these potentials are yet unpublished we describe them in some details. We have used a Lennard–Jones type pair potential for the He–C interaction. Such an attractive potential has been chosen in light of recent calculations [16]. The He–Si interaction is described by a Buckingham potential. Both potentials read as follow:

$$v(\text{He–Si}) = A \exp\left(-\frac{r_{\text{He–Si}}}{\rho}\right) \quad (2)$$

and

$$v(\text{He–C}) = \frac{A}{r_{\text{He–C}}^{14}} - \frac{B}{r_{\text{He–C}}^6} \quad (3)$$

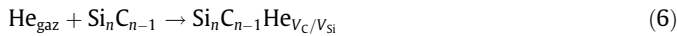
The parameters of both potentials have been fitted on previously calculated ab initio data [15] on helium insertion energies in vacancies (V_{Si} and V_{C}) and interstitial sites (T_{C} and T_{Si}) in silicon carbide. The insertion energies E_{ins} of helium (at 0 K) have been defined by writing the following equation for interstitials (T_{C} or T_{Si}):



with

$$E_{\text{ins}}^{T_{\text{C}}/T_{\text{Si}}} = E(\text{Si}_n\text{C}_n\text{He}_{T_{\text{C}}/T_{\text{Si}}}) - E(\text{Si}_n\text{C}_n) - E(\text{He}_{\text{gaz}}) \quad (5)$$

The equations for vacancies read a similar way as:



with

$$E_{\text{ins}}^{V_{\text{C}}/V_{\text{Si}}} = E(\text{Si}_n\text{C}_{n-1}\text{He}_{V_{\text{C}}/V_{\text{Si}}}) - E(\text{Si}_n\text{C}_{n-1}) - E(\text{He}_{\text{gaz}}) \quad (7)$$

We have used in the fitting procedure the same 64 atom cells as in ab initio calculations. The optimal set of parameters is given in Table 1. The insertion energies of helium calculated with empirical potentials (Table 2) reproduce quite well the ab initio data obtained by Van Ginhoven et al. [15]. In order to cross-check the quality of the present potentials for helium, we have calculated the activation energies for interstitial helium migration and for helium de-trapping from the vacancy sites (see Table 2). Again, the empirical potentials agree well with the activation energies for migration obtained with ab initio data, the difference between the empirical potentials and the ab initio data lying around 20%.

Table 1

Parameters of the pair potential interaction for He–C et He–Si fitted to the ab initio insertion energies calculated by Van Ginhoven et al. [15].

	A (eV Å [14])	B (eV Å [6])
He–C (Lennard–Jones)	6333.435553	23.842031
	A (eV)	ρ (Å)
He–Si (Buckingham)	14.647429	0.547926

Table 2

Comparison between empirical potentials and ab initio [15] insertion energies and activation energies of single helium in silicon carbide. Insertions energies (italic) have been used for the fitting, the activation energies (regular type) have been used to cross-check the quality of the potentials.

Energies (eV)	Emp. Pot.	Ab initio [15]
$E_{\text{ins.}}(T_{\text{C}})$	2.70	2.71
$E_{\text{ins.}}(T_{\text{Si}})$	1.51	1.51
$E_{\text{ins.}}(V_{\text{C}})$	1.63	1.62
$E_{\text{ins.}}(V_{\text{Si}})$	0.88	0.86
$E_{\text{act.}}(T_{\text{C}} \rightarrow T_{\text{Si}})$	0.9	1.3
$E_{\text{act.}}(T_{\text{Si}} \rightarrow T_{\text{C}})$	2.1	2.5
$E_{\text{act.}}(V_{\text{C}} \rightarrow T_{\text{C}})$	0.8	0.6
$E_{\text{act.}}(V_{\text{Si}} \rightarrow T_{\text{C}})$	0.5	0.4

2.2. Generation of the cavities and insertion of He atoms

Our crystal structure is βSiC (cubic). We considered series of spherical vacancy aggregates centered on a silicon atom. Each aggregate can be denoted by the number of atoms that were removed or by the radius of the associated cavity (quoted R_{c}) which we define as the distance between the center and the closest remaining atom. The helium atoms are inserted in the cavities along a face-centered cubic network starting from the center and adding additional shells of atoms. This initial He atomic structure is systematically quenched and then thermalized for a few ten pico-seconds. Constant temperature calculations are performed thanks to a Langevin thermostat.

2.3. Methodology of free energy calculation

To calculate the free energies of He atoms in vacancy aggregates and in interstitial positions, we use an usual disintegration procedure [17], that we recall below.

The interaction of a selected helium atom with all the other constituents is reduced at each time step of the MD simulation (thus creating, step by step, a “ghost” atom of helium which is, in our situation, tantamount to disintegrate this atom). If the helium atom is disintegrated slowly (the rate of disintegration is small), the surrounding atoms are not much affected at each step: the transformation is then quasi-static (or reversible). In such transformation, during a step of disintegration we can assume that there is no creation of entropy ($\delta S_{\text{created}} = 0$). So we have: $dS = \delta S_{\text{exchanged}}$ ($\delta S_{\text{exchanged}}$ is the entropy which is exchanged with the thermostat during a step), which gives:

$$dU = dF + T\delta S_{\text{exchanged}} = dF + \delta Q_{\text{reversible}} \quad (8)$$

where $\delta Q_{\text{reversible}}$ is the little variation of heat during the reversible transformation. Yet, the variation of internal energy during a reversible reaction is given by:

$$dU = \delta Q_{\text{reversible}} + \delta W_{\text{reversible}} \quad (9)$$

From (8) and (9), we get:

$$\Delta F = \int \delta W_{\text{reversible}} \quad (10)$$

where the integral proceeds along the disintegration path. This integral is equal to the free energy of the disintegrated atom. Thus, during each MD step, we determined the work generated by the reduction of the interactions. And finally, the integration of the work along the disintegration path gives us the free energy of the removed helium. The quality of the procedure depends on the slowness of the disintegration. The slower the disintegration, the better the approximation of chemical potential, because $\delta S_{\text{created}}$ tends towards 0. At the opposite, if the disintegration rate is too high, the system is

greatly disturbed and the error on the free energy cannot be neglected ($\delta S_{created}$ being not negligible).

It is worth noting that drawbacks are known for the present disintegration procedure. Indeed it is known that disintegration–insertion procedures (such as the Widom procedure or the path sampling procedure) are more accurate [17,18]. However we chose not to use these more involved methods for two reasons. First, these procedures are generally heavier as they include series of insertions and disintegrations and we are in the present paper only interested in qualitative trends that we believe are obtained with a simple disintegration procedure. Second, our case is somehow particular as we are interested in the free energy of He atoms inside a *specific portion of the simulation box* (i.e. the cavity) and not on the chemical potential of He in the *whole box*, as it is usually the case in free energy calculations. If series of disintegration–insertion of an He atom are performed, it is not possible to guarantee that this atom is reinserted in the right portion of the box and one end up with the chemical potential of the He atom in the whole box which is not what we are interested in.

In practice the disintegration is performed in 20 000 iterations of .2 fs each, i.e. in 4 ps. Such fast disintegrations proved enough to get the qualitative trends we are interested in.

Table 3
Free energy of an He atom in tetrahedral interstitial position surrounded by Si (T_{Si}) or C (T_C) atoms.

He free energy (eV)	T_{Si}	T_C
300 K	1.59	2.72
1000 K	1.68	2.88
2500 K	2.12	Unstable

3. Results

3.1. Free energy of He atom in interstitial sites

To compare the free energies of He atoms in the cavities with He in the bulk of SiC, we first calculated the free energies of interstitial He in two possible sites: the tetrahedral sites surrounded by Si or C atoms (T_{Si} and T_C respectively). The values of the free energies for these two sites at 300 K, 1000 K and 2500 K temperatures are given in Table 3. Two points are worth noting. First the silicon interstitial site is the most stable site at all temperature in agreement with what was calculated at 0 K (see above part I.). Second, at 2500 K the carbon interstitial site is unstable in the sense that the inserted helium atom quickly moves from this site to a neighboring silicon interstitial site.

The difference in free energy between the position in the bulk and in the cavity is therefore:

$$\delta = F_{bubble}^{He} - F_{T_{Si}}^{He} \quad (11)$$

if $\delta < 0$, helium atoms are in an energetically favored position in the cavity; if $\delta > 0$, helium atoms are in an energetically un-favored position in the cavity; $\delta = 0$ corresponding to a perfect energetic equilibrium between He atoms in the cavity and in interstitial positions in the bulk.

3.2. Free energy of He atoms inside nanoscale cavities

We had to restrict to extremely small cavities due to computational limitations. Indeed a somewhat large dispersion of the obtained free energies is observed (see Figs. 1–3). Therefore one has to calculate the free energy of *every* He atom in a cavity, i.e. perform independent disintegrations of every He atom. This of course

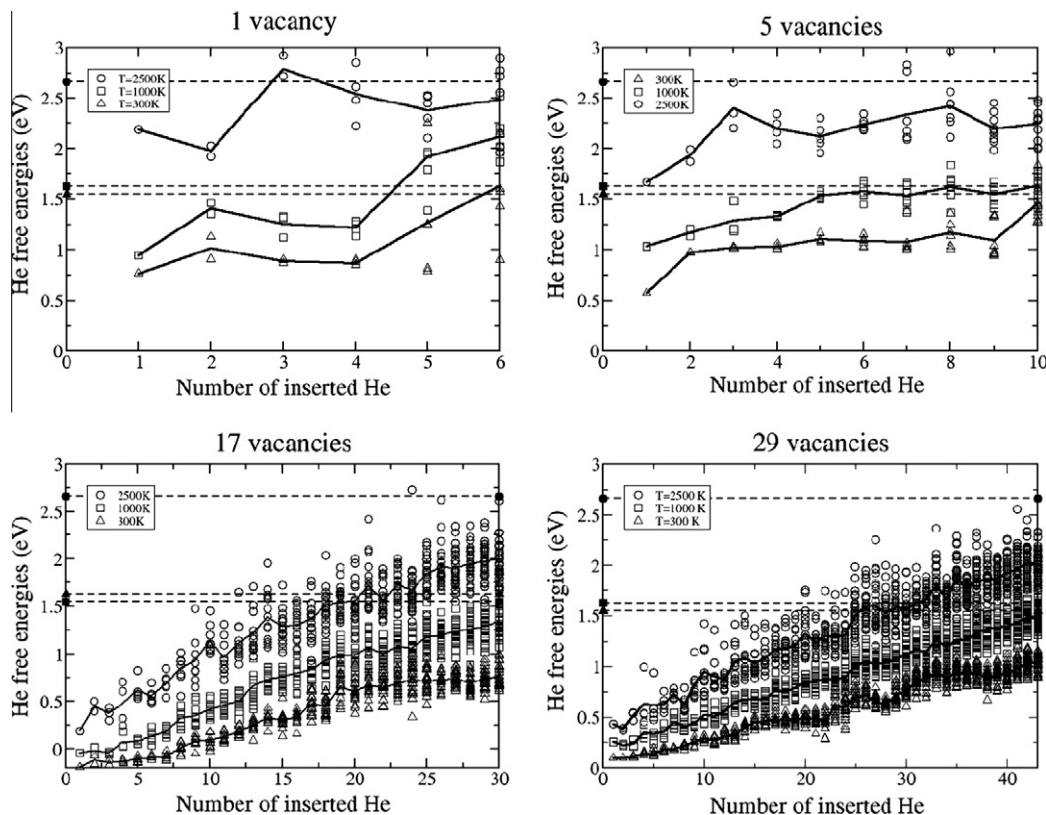


Fig. 1. Free energies of He atoms inserted in sub-nanoscale cavities made of 1, 5, 17 and 29 vacancies at 300 K, 1000 K and 2500 K. Continuous lines indicate the averages over the inserted helium atoms. Dashed horizontal lines indicate He free energy values in the bulk (in the T_{Si} site).

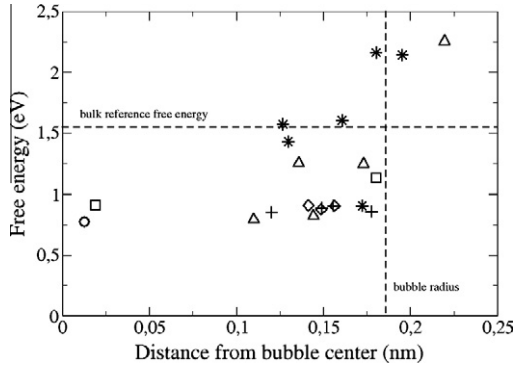


Fig. 2. Distance from bubble center and free energy of 1 (resp. 2, 3, 4, 5, 6) He atoms in a mono-vacancy cavity at 300 K: circle (resp. squares, diamonds, crosses, triangles and stars). The horizontal line indicates the free energy of an He atom in a bulk Si-interstitial site. The vertical line indicates the border of the cavity.

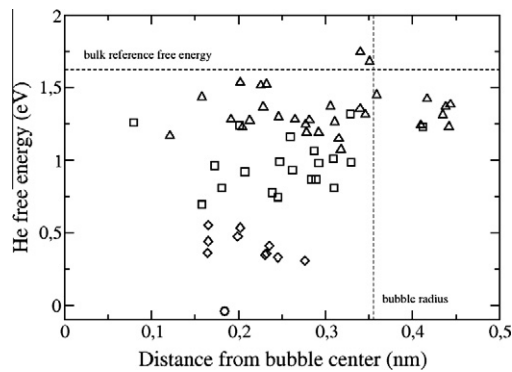


Fig. 3. Distance from bubble center and free energy of 1 (resp. 10, 20, 30) He atoms in a 17 vacancy cavity at 1000 K: circle (resp. diamonds, squares, triangles). The horizontal line indicates the free energy of an He atom in a bulk Si-interstitial site. The vertical line indicates the border of the cavity.

strongly limits the number of He one can consider. In this part, cavities made of 1, 5, 17 and 29 vacancies (centered on a Si atom) are considered. For each cavity up to $N_{\text{inserted}}^{\text{max}} = 6, 10, 30$ and 43 He atoms are inserted, respectively, i.e. all possible numbers of He atoms in the bubble from 1 to $N_{\text{inserted}}^{\text{max}}$ were considered. In each case the box is thermalized and then the free energy of every He atom is calculated. Three temperatures were considered: 300, K, 1000 K and 2500 K. All in all that amounts for each cavity to $3 \times N_{\text{inserted}}^{\text{max}}$ MD thermalization runs and $3 \times N_{\text{inserted}}^{\text{max}} \times (N_{\text{inserted}}^{\text{max}} - 1)/2$ MD integrations runs to calculate the free energies.

Before tackling the values of the free energies, we shall expose the spatial repartition of the He atoms after relaxation at the various temperatures. When very few He atoms are inserted in the cavities they all remain inside the bubble far from its border. Upon accumulation He atoms start to get further away from the center. It proves quite difficult to properly define the interior of the bubble or its border. In lack of a better definition, we chose, by convention, to flag an He as gone out of the cavity when its distance from the center exceeds (at the end of the thermalization run) the radius of the cavity R_c (as defined above except for the five vacancy cavity where the common definition of the radius proves inappropriate and R_c is reduced by 0.02 nm). With this definition one observes that beyond a certain amount of inserted He, not all of them remain inside the cavity and some are ejected outside of it (see Figs. 2 and 3). We found that the number of He atoms that remain inside the cavity after thermalization clearly saturates. We note $N_{\text{inside}}^{\text{max}}$ this maximum number of He atoms that remain inside the cavity.

Table 4

Equilibrium number of He atoms in sub-nanocavities (see text for details). Numbers in regular type (resp. italics) indicate that the estimation is based on $N_{\text{inside}}^{\delta=0}$ (resp. $N_{\text{inside}}^{\text{max}}$).

N_{Vac}	Radius (nm)	Equilibrium number of He atoms		
		300 K	1000 K	2500 K
1	0.186	4	3	3
5	0.303	6	5	7
17	0.355	23	24	22
29	0.428	34	35	37

Turning now to the calculated values of the free energies, one first observes a somewhat large spread of the values. However one satisfactorily obtains, as expected, that the average He free energies in the cavities (lines in Fig. 1) increases with the amount of He in the cavities as well as with temperature.

When few He atoms are inserted, their free energy proves much lower than the reference free energy of He in interstitial bulk positions. Upon accumulation of He atoms in the cavity, the average free energy increases. In most cases the first He ejection from the cavity takes place while all He atoms still have a lower free energy than in the interstitial sites (see Figs. 2 and 3). Ejection thus takes place before the free energy of He atoms inside the cavity reaches the value experienced by He interstitials in the bulk. Further accumulation of He atoms leads to an increase of their free energies, be they inside or outside the cavity. The free energies get closer and closer to the bulk values. In some cases we considered large enough amounts of inserted He atoms to reach the point where the free energy of one or many He atoms do reach the bulk interstitial value. These first He atoms having a higher free energy than in the bulk may be either in the cavity or outside it. In this last case further accumulation is needed to possibly reach the point where an He atom inside the cavity exhibits a higher free energy than the bulk reference. At this point the number of He inside the cavity has exceeded its equilibrium value. We then denote $N_{\text{inside}}^{\delta=0}$, the maximum number of He atom inside the cavity for which none of them has a higher energy than the bulk reference. $N_{\text{inside}}^{\delta=0}$ is the number of He atoms in the cavity when equilibrium is set between the bubble and the bulk.

We thus have two ways of estimating the number of He atoms in the bubble at equilibrium. First when enough He atoms were inserted to reach the inversion of equilibrium between inside the bubble and in the bulk, one has access to $N_{\text{inside}}^{\delta=0}$ which is the correct measure of the equilibrium number of He in the bubble. Second even when this inversion point is not reached one still observes an overall saturation of the number of He atoms that remain inside the bubble to the $N_{\text{inside}}^{\text{max}}$ value. Using $N_{\text{inside}}^{\delta=0}$ when available and $N_{\text{inside}}^{\text{max}}$ in the other case we indicate in Table 4 the maximum number of He atom that can be accommodated in a bubble as a function of temperature and size of the cavity.

4. Discussion

Before discussing our results we should remind the reader that we are primarily interested in the number of He atoms that would sit inside a cavity if the full thermodynamical equilibrium was achieved. In reality such equilibrium is very difficult to achieve and kinetic factors (such as the diffusion of He atoms from the bulk to the cavities) affect the number of He atoms in a cavity. We do not tackle in this paper these kinetic factors, as we restrict ourselves to the pure thermodynamical equilibrium.

The free energy calculations allow us to further discuss the behavior of He atoms inside cavities in SiC. The initial assumption behind these calculations was that upon accumulation of He

atoms inside a bubble, their free energies would increase up to reach the value experienced by He interstitials in the bulk at which point the bubble would have reached its equilibrium He content. Calculations have shown the actual situation to be more complex. First the implicit assumption that He atoms would always remain inside the bubble proves wrong. For a certain amount of He atoms inside the bubble some are ejected outside of it. The first He atoms pushed away from the bubble end up in interstitial sites close to the surface in which they have a lower free energy than in the bulk. Upon accumulation of He, these interstitial sites close to the surface get more and more occupied and their free energies rise. This difference in free energy of interstitial sites close to the cavity with respect bulk interstitial sites relates to a sub-surface segregation process making the interstitial sites close to the surface energetically favorable compared to the bulk sites. The chemical interactions of He with its surroundings being weak, this shift in energy is mainly due to elastic effects related to the local dilatation of the SiC lattice close to the surface of the cavity. Indeed we checked that interstitial He atoms in dilated crystal structures exhibit a lower free energy than at equilibrium volume.

The existence of this sub-surface segregation complicates the picture of equilibrium between an He bubble and bulk interstitials. Indeed, equilibrium between the bubble and bulk interstitials is achieved when the free energies of He atoms are equal throughout the system which implies that:

- He atoms inside the bubble should have a free energy equal to the reference bulk value;
- He atoms outside but close to the bubble should also have the same free energy.

This last condition is achieved with a higher local concentration of He atoms close to the surface than in the bulk. One would finally get a concentration gradient from the surface of the bubble to the bulk with higher concentrations at the surface side. Present calculations show hints of the existence of this concentration gradient at full equilibrium and evidence that the He content associated with a cavity includes not only He atoms inside the bubble but also those segregated in the material close to the cavity. However the precise determination of this concentration gradient goes far beyond the scope of the present paper. In particular simple thermodynamical arguments prove that the concentration gradient should be more intense close to smaller cavities than in the vicinity of larger cavi-

ties (this is the Gibbs–Thompson effect). Unfortunately we were unable to find clear evidence of this phenomenon.

We now come back to the effect of temperature on the amount of He that can be accommodated in a given bubble. Our calculations show clearly that for low amount of He atoms, the free energy of He atoms in a bubble is increasing with temperature. However the number of He inside a bubble at equilibrium with the bulk is remarkably constant with temperature for these very small cavities (Table 4).

5. Conclusion

In this paper we have studied from the thermodynamic point of view the equilibrium of He in sub-nanoscale cavities in SiC by calculating free energies for He atoms vacancy aggregates. This highlighted the existence of a sub-surface segregation in interstitial sites close to the surface of the cavity. The He content associated with a cavity therefore includes not only He atoms inside it but also those segregated in the material close to it.

Finally, the number of helium in sub-nanoscale cavities is almost independent from temperature which confirms the relevancy of the ab initio approaches which neglect the temperature effect for sub-nanoscale cavities.

References

- [1] P. Jung, H. Klein, J. Chen, *J. Nucl. Mater.* 283–287 (2000) 206.
- [2] A. Hasegawa, M. Saito, S. Nogami, K. Abe, R.H. Jones, H. Takahashi, *J. Nucl. Mater.* 264 (1999) 355.
- [3] T.S. Duh, K.M. Yin, K.Y. Yan, P.C. Fang, C.W. Chen, J.J. Kai, F.R. Chen, Y. Katoh, A. Kohyama, *J. Nucl. Mater.* 329–33 (2004) 518.
- [4] J.R. Cost, K.Y. Chen, *J. Nucl. Mater.* 67 (1977) 265.
- [5] R.S. Barnes, *J. Nucl. Mater.* 11 (1964) 135.
- [6] C.C. Fu, F. Willaime, *Phys. Rev. B. Condens. Matter.* 72 (2005) 064117.
- [7] L. Yang, X.T. Zu, F. Gao, *Phys. B-Condens. Matter.* 403 (2008) 2719.
- [8] O. Runevall, N. Sandberg, *J. Phys.-Condens. Matter.* 21 (2009).
- [9] L. Porter, J. Li, S. Yip, *J. Nucl. Mater.* 246 (1997) 53.
- [10] J. Li, L. Porter, S. Yip, *J. Nucl. Mater.* 255 (1998) 139.
- [11] J.P. Crocombette, F. Gao, W.J. Weber, *J. Appl. Phys.* 101 (2007) 023527.
- [12] J.P. Crocombette, L. Gelebart, *J. Appl. Phys.* 106 (2009) 083520.
- [13] K.T. Tang, J.P. Toennies, *J. Chem. Phys.* 118 (2003) 4976.
- [14] W.G. Scheider, J.A.H. Duffie, *J. Chem. Phys.* 17 (1949) 751.
- [15] R.M. Van Ginhoven, A. Chartier, C. Meis, W.J. Weber, L.R. Corrales, *J. Nucl. Mater.* 348 (2006) 51.
- [16] T.S. Jakubov, D.E. Mainwaring, *Adsorp.-J. Int. Adsorp. Soc.* 14 (2008) 727.
- [17] D. Frenkel, B. Smit, *Understanding Molecular Simulation*, Academic Press, San Diego, 2002.
- [18] M. Athenes, *Eur. Phys. J. B* 38 (2004) 651.