On phase diagrams for Au-Si nanosystems: thermodynamic and atomistic simulations

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Abstract. Phase diagrams for Au-Si nanosystems were calculated by using thermodynamic simulation (NANOCALPHAD methodology) and molecular dynamics (MD). Thermodynamic simulations have been carried out for two Au-Si nanosystems: (i) a solid (crystalline) Si or Au nanoparticle (NP) contacting with an Au-Si nanodroplet of the same radius; (ii) a cylindrical Si nanowire (nanowhisker) with an Au-Si nanodroplet on its butt. We have found that the eutectic temperature of the first system decreases in comparison with the bulk eutectic temperature, and the position of the eutectic point slightly shifts to a lower value of the molar fraction of Si that agree with MD results obtained on another system, i.e. on spherical Au-Si NPs. Contrary to the first system, the eutectic temperature of the second one, i.e. of the system “Si nanowhisker – Au-Si nanodroplet” increases in comparison with the bulk phase diagram. An explanation of such a result is proposed and discussed.

1. Introduction

It is difficult to overestimate importance of phase diagrams of binary and multicomponent alloys for development of methods of fabrication of nanoparticles (NPs) and optimization of their properties. Traditionally, phase diagrams of bulk alloys are obtained by employing the thermometry, i.e. by plotting the cooling curves of the corresponding melt. Thermometric data are supplemented by the X-ray diffraction and other methods to analyze the phases arisen during the solidification of the melt. It is quite natural that attempts were made and are being made to construct phase diagrams for NPs and other low-dimensional objects [1], including phase diagrams for binary Au-Si nanosystems [2–4]. At the same time, the experimental determination of phase diagrams for NPs and other nanoscale objects, such as nanowhiskers, is very difficult. In this regard, the data available in literature, including phase diagrams for Au-Si nanoalloys [2–4], were not obtained experimentally but extending conventional (bulk) CALPHAD [5] to nanosystems. The degree of validity of such an extension, the unambiguity and even the correctness of applying the concept of the phase diagram to low-dimensional systems remain not entirely clear. Usually the CALPHAD method is used by employing one of the well-known professional programs. First of all THERMOCALC should be mentioned. However, in most cases it remains unclear how some authors, including the authors of papers [3, 4], extend this program to nanosized objects. As a rule, before considering nanosystems, the authors of papers on NANOCALPHAD calculate phase diagrams of the corresponding bulk phases as well that may be treated as validation of the following...
extensions to nanosystems. According to [3], the phase diagram of the Au-Si nanosystem “crystalline Si NP – Au-Si nanodroplet of the same radius” keeps its overall shape of the eutectic type phase diagram but the eutectic temperature $T_e$ decreases and the eutectic point somewhat shifts to the left, i.e. towards a lower content of Si, and this decrease of $T_e$ is of about 70 K. However, in [2, 4] a noticeable eutectic temperature depression was not revealed.

The main objects of our thermodynamic study are two types of Au-Si nanosystems: (i) a solid (crystalline) Si or Au NP contacting with an Au-Si nanodroplet of the same radius; (ii) a cylindrical Si nanowire (nanowhisker) with an Au-Si nanodroplet on its butt (Figure 1). The interest in Au-Si nanoalloys has determined by the prospects for their application in nanoelectronics and other directions of nanotechnology. In particular, Au nanodroplets are used as catalysts (seeds) for growing Si nanocrystals, including Si whiskers [6], and for the further development of methods of fabrication of Si nanocrystals, some open questions should be answered. The main applied problem related to Au-Si phase diagram aimed to applications in the alternative silicon nanoelectronics which does not involve macroscopic Si single crystals.

Figure 1. Schematic presentation of two types of nanosystems for which phase diagrams were calculated employing NANOCALPHAD: (a) spherical crystalline Si or Au NP – Au-Si nanodroplet of the same radius $R$; (b) cylindrical Si nanowhisker – Au-Si nanodroplet.

Obviously, for the first time in this work, the phase diagram for Au-Si NPs was also constructed by using the results of molecular dynamics (MD) simulation. However, in the next section and in Section 4 it is elucidated that interpretation of the phase diagram in our MD experiments differs from that in the thermodynamic simulation based on NANOCALPHAD.

2. Molecular dynamics approach to calculation of the phase diagram for the Au-Si nanoalloy

The above-mentioned experimental approach to constructing bulk phase diagrams relates to the cooling curves which allow to identify all the solid-state structures arising in the system during its cooling. At the first sight, the same method can be employed in MD experiments on NPs. However, in MD experiments formation not only of a solid equilibrium nanophase but also of a precursor of the crystalline nucleus during the cooling of the melt can require long relaxation times, which cannot be achieved in computer experiments. At the same time, for Au-Si nanoalloys one hardly should expect appearance of some specific solid structures aside from fcc Au and diamond Si. Besides, according to [7], Si and Au are characterized by negligible mutual solubility in the solid state. Obviously, for such alloys both cooling a nanodroplet and heating a solid NP until completion of the melting process can be used to obtain the phase diagram for the nanoalloy.

We have used the isothermal MD (the Nose-Hoover thermostat) by employing the well-known open program LAMMPS. As was established earlier [8, 9] in our MD experiments on single-component Si nanodroplets, described by the Stillinger-Weber potential [10], these droplets do not crystallize during the relaxation times available in computer experiments (up to 100 ns). However, for binary nanosized
Au-Si NPs described by the Angular Dependent Potential (ADP) [11], a hysteresis loop is observed during the heating – cooling cycles (see figure 2), similar to the melting – crystallization hysteresis loop for metal NPs [12–14]. Accordingly, temperature of the melting completion (point A in figure 2) can be considered as the liquidus temperature. So, the temperature of liquidus was registered similar to registration of the melting temperature of single component Si [9, 10] and metal [12, 13] NPs, i.e. by observing the upward jump in the heating curve (point A in curve 2 presented in figure 2). The liquidus line constructed in this way is presented by dots in figure 3 (x is the molar fraction of Si).

**Figure 2.** Temperature dependence of the specific cohesive energy of a Au$_{18}$Si$_{1003}$ NP, demonstrating the melting-solidification hysteresis: 1 - heating curve, 2 - cooling curve.

**Figure 3.** Comparison of the phase diagram obtained from the results of our MD experiments on Au-Si NPs containing 2000 atoms (dots correspond to the liquidus line) with the experimental phase diagram of the bulk Au-Si alloy [7] shown by the solid line. The definition of the reduced temperature $T^*$ is explained in the text of the paper. Dashed lines correspond to the solidus lines.

As it is noted in [11], where the employed parameterization of the ADP potential is proposed, this parameterization much better reproduces properties of Au-Si alloys than of pure components (Au and Si). Indeed, this potential gives underestimated bulk values of the melting temperatures $T_{m,Au}$ and $T_{m,SI}$ of both Au and Si single-component NPs. Accordingly, for a more adequate comparison of our MD phase diagram for Au-Si NPs of radius 2 nm with the bulk experimental phase diagram [7], the reduced temperatures $T^*$ in figure 2 is interpreted as $T/T_{m,SI}$ for NPs and as $T/T_{m,SI}^{(\infty)}$ for the bulk alloy where $T_{m,SI}$ is the melting temperature of Si NPs of the chosen size and $T_{m,SI}^{(\infty)} = 1685$ K is the bulk melting point of Si [7]. According to figure 3, the reduced value of the eutectic temperature for the nanoalloy $T_{e}^{(n)} \approx 0.32$ is less than the bulk reduced eutectic temperature $T_{e}^{(\infty)} \approx 0.4$. Taking into account that $T_{m,SI}^{(\infty)} = 1685$ K and $T_{m,SI} = 1200$ K [8, 9], we find $T_{e} = 384$ K that is by 252 K lower than the experimental value of the bulk eutectic temperature $T_{e}^{(\infty)} = 636$ K [7]. At the same time, the eutectic point of the nanoalloy corresponds to $x_{e} = 0.1$ whereas for the bulk alloy $x_{e}^{(\infty)} = 0.2$, i.e. $x_{e} < x_{e}^{(\infty)}$. The conclusion about the depressions of $T_{e}$ in comparison with $T_{e}^{(\infty)}$ and of $x_{e}$ in comparison with $x_{e}^{(\infty)}$ is consistent with thermodynamic results [3, 4]. At the same time, in [3] the $T_{e}$ depression for NPs of 10 nm in size was found to be about 70 K, i.e. much lower. However, the results of paper [4], where NANOCAHELPHAD was also used, predict that the eutectic temperature $T_{e}$ of the solid Si or Au NP – liquid Au-Si nanodroplet system practically coincides with the bulk value $T_{e}^{(\infty)}$ (both NP and
nanodroplet were of 14 nm in size). Then, contrary to our MD results and results of papers [3, 4], in [2], any shift in the position of the eutectic point in their graph is not noticeable. Moreover, the diagrams for NPs and for the bulk phase noticeably differ only at \( x \ll x_e \) and \( x \gg x_e \), only, i.e. when \( x \) approaches to zero or to unity.

3. Thermodynamic approach to design of phase diagrams for Au-Si nanoalloys

When extending the CALPHAD methodology [5] to nanosystems, we cannot consider a separate NP of a nanoalloy as it was done in the course of our above MD simulation (see also Sec. “Discussion”). In other words, the existing methodology presumes the thermodynamic equilibrium between two objects, e.g. between a solid NP and a nanodroplet. No doubt that such phase diagrams are of interest from both scientific and applied points of view. However, one should take into account that the NANOCALPHAD phase diagram for a definite nanoalloy, e.g. for the Au-Si nanoalloy, is not unambiguous. Thermodynamic simulation of the phase diagram for the system presented in figure 1a, i.e. for the system consisting of a solid Si or Au NP contacting with an Au-Si nanodroplet, is of special interest as the available theoretical results, presented in [2–4], are rather ambiguous, though the authors of these works used similar NANOCALPHAD algorithms. Moreover the authors of [3, 4] used the same commercial program THERMOCALC adapting it, in some way, to nanoscale objects. In this regard, it is desirable to compare the NANOCALPHAD results [2–4] and our MD results with our own thermodynamic simulation results obtained not employing the THERMOCALC program. We did not possess this program. Besides, we are not sure that it would be quite correct to employ it for nanosystems at least before some disputable problems of NANOCALPHAD will be, to a lesser or greater extent, solved.

In general our approach, developed following to official CALPHAD algorithms [5], is more similar to [2, 3] than to [4], as we did not employ the activity coefficients and used the Redlich-Kister equation to find the Gibbs energy of mixing. The bulk phase diagram was also calculated to verify our algorithms and our computer programs based on this algorithm as well as to verify the involved parametrization. Algorithms for constructing the phase diagram of the bulk Au-Si alloy is illustrated in figure 4: for a given temperature it is necessary to find the derivative \( \partial G / \partial x \) of the Gibbs energy \( G \) of the system with respect to the molar fraction \( x \) of the second component. The derivative in question is determined via the slope of the dashed straight line shown in figure 4. In fact such a procedure corresponds to determination of the chemical potentials of components from the integral Gibbs energy of the whole system, and the above algorithm is adequate to the eutectic-type alloys if in the solid state components A and B are characterized by the negligible mutual solubility. It is just the situation that is relevant to the eutectic Au-Si system [7].

![Figure 4. To explanation of the algorithm of thermodynamic simulation.](image-url)
The Gibbs energy of the binary A-B melt nanodroplet can be presented as follows

\[ G_L = x \mu_{B,L}^{(0)} + (1 - x) \mu_{A,L}^{(0)} + RT \left[ x \ln x + (1 - x) \ln (1 - x) \right] + G_L^{(\text{mix})} + G_L^{(S)} \]  

(1)

where \( x \equiv x_B \) (subscript B corresponds to solid Si or Au NP), \( \mu_{A,L}^{(0)} \) and \( \mu_{B,L}^{(0)} \) are the molar chemical potentials of the bulk phases of components A and B in the liquid state, \( G_L^{(\text{mix})} \) is the Gibbs energy of mixing and \( G_L^{(S)} \) is the surface term into the Gibbs molar energy of the nanodroplet (\( \sigma_L \) is the surface tension of the melt of the chosen composition, \( r \) is radius of both the Au-Si nanodroplet and Si or Au solid NP contacting with the droplet). For the bulk phase in the standard state \( G_L^{(S)} = 0 \). Here and after subscript \( L \) corresponds to the liquid nanodroplet. The solid Si or Au NP of the same radius (figure 1a) or the Si nanowhisker (figure 1b) will be denoted by the subscript S. The surface term into the Gibbs molar energy of the solid Si or Au NP will be presented by the next analogous equation

\[ \sigma_S^{(S)} = 2 \sigma_L V_L / r \]  

(2)

where the multiplier \( 2 \sigma / r \) has the sense of the additional (capillary) pressure [14]. For the nanowhisker, having the cylindrical shape, the multiplier \( “2” \) in equation (3) will be eliminated, i.e.

\[ \sigma_{LA}^{(S)} = 2 \sigma_L V_L / r, \sigma_{LS}^{(S)} = \sigma_S V_S / r . \]  

(4)

Then, following to [2, 3], the Gibbs energy of mixing \( G_L^{(\text{mix})} \) was found by using the Redlich-Kister equation with the four terms of expansion:

\[ G_L^{(\text{mix})} = x(1 - x) \sum_{i=0}^{3} L_i (1 - 2x)^i \]

where \( L_i \) are the expansion coefficients. Their values, as well as the values of the most of other parameters, necessary for calculations, except the surface tensions, were taken from [3] where corresponding references are given.

Reliable data on the surface parameters are much less available. Thus, there are some experimental data [15] on the surface tension \( \sigma_L \) of the Au-Si melt. Besides, \( \sigma_L \) can be calculated employing the Butler equation as it was done in [3]. At the same time, in [3] it is noted that the simple linear approximation

\[ \sigma_L = (1 - x) \sigma_L^{(A)} + x \sigma_L^{(B)} \]  

(5)

also gives fairly good results for \( \sigma_L \) where \( \sigma_L^{(A)} \) and \( \sigma_L^{(B)} \) are the surface tensions of components. It is noteworthy that, a small deviation of \( \sigma_L \) from the dependence (5) to higher values was found in [3] employing the Butler equation whereas experimental data [15] demonstrate a bent into the opposite direction. For this reason we have decided to employ equation (5). The values of \( \sigma_L^{(A)} \) and \( \sigma_L^{(B)} \) for the pure Au and Si melts, respectively, as well as of their temperature derivatives were taken from review [16]. The experimental value of the surface tension of the solid Si was taken from [17] and of the solid Au from [16].

The bulk phase diagram (the liquidus line only) is depicted in figure 5 by the thick solid line 1. The liquidus line was calculated, as it is usually done, assuming that the chemical potential of one of the components in the melt coincides with the chemical potentials of the bulk solid phase: the Au phase (the left branch) or the Si one (the right branch). Such an algorithm takes into account that when \( x < x_e \) the solid Au inclusions only can precipitate from the Au-Si melt and when \( x > x_e \) the precipitation of the solid Si diamond phase takes place in the corresponding two-phase region. Our phase diagram for the bulk alloy obtained by means of the thermodynamic simulation practically coincides with the
The solidus lines are not shown in figure 5 as they correspond to horizontal lines drawn through the eutectic points.

The liquidus line presented by curve 2 in figure 5 corresponds to the system shown in figure 1a, i.e. to equilibrium between an Au-Si nanodroplet of the given radius and the solid Au or Si NP of the same radius: Au NP for $T < T_e$ and Si NP for $T > T_e$, respectively. Curve 3 represents the liquidus line for the system shown in figure 1b, i.e. for the Si whisker with the Au-Si droplet on its butt. The sense of the curve 4 in figure 5 will be commented in the next section.

**Figure 5.** Comparison of the phase diagrams for the bulk Au-Si alloy obtained involving the CALPHAD method (curve 1 corresponds to the calculated bulk liquidus line) with the phase diagrams calculated for some nanosystems on the basis of the Au-Si nanoalloy: curve 2 (dashed line) corresponds to equilibrium between the Au-Si nanodroplet contacting with its the solid Si or Au NP of the same radius $r = 5$ nm; curve 3 (dotted line) corresponds to the Si whisker with the Au-Si nanodroplet on its butt proposing that the whisker radius $r = 5$ nm coincides with the droplet radius (see figure 1b). Curve 4 is commented in the next section.

**4. Discussion**

Thus, obviously for the first time, we obtained the phase diagram of the Au-Si nanoalloy presented in section 2 (figure 3) by employing the MD method. One can see that the dots in this figure are characterized by large enough scattering and demonstrate not quite regular behavior. The methodology for constructing this phase diagram differs from the generally accepted experimental technique based on analysis of the cooling curves. However, as some precursors of the crystalline nuclei in nanodroplets are arising and growing slowly enough relative to times of order of 100 ns available in MD simulations, the liquidus line in figure 3 is obtained by means of heating crystalline NPs instead of cooling nanodroplets till the first appearances of the crystallinity. The most important MD result is the significant eutectic temperature depression (by about 250K for Au-Si NPs of radius $r = 2$ nm). Besides, the eutectic point in figure 3 is significantly shifted to $x = 0.1$ in comparison with the bulk eutectic point ($x = 0.2$).
We believe that our MD results under discussion are no doubt of interest though the problem of constructing phase diagrams for nanosystems employing MD simulations is far from its complete relevant solution. In particular, so large depression of $T_e$ can be overestimated.

For this and a number of other reasons, the thermodynamic simulation of phase diagrams for nanosystems is of special interest, and this direction of the thermodynamic simulation may be treated as an extension of CALPHAD to nanosystems. Such an extension is often referred to as NANOCALPHAD. Specific features of NANOCALPHAD in comparison with the conventional CALPHAD method as well as some related problems, including extension of the Gibbs phase rule to nanosystems, are considered in interesting, as we believe, review by Kaptay [1]. However, not only extension of CALPHAD to nanosystems provokes a number of open questions but also the notion of the phase diagram itself when extended to nanosystems. Really, as it has been already mentioned, experimentally the bulk phase diagrams are obtained by means of cooling the melted alloy. When some solid precipitates are registered, a dot in the liquidus line is fixed. In the frames of the CALPHAD method, the thermodynamic equilibrium between the bulk melt and the bulk solid is considered. So, the precipitates in question are treated as bulk phases, and usually corresponding calculations demonstrate surprisingly good agreement with experimental phase diagrams. Presumably, in part so ideal agreement is provided by some empirical adjustments of thermodynamic parameters figuring in the equation for the Gibbs energy of the alloy. For nanosystems direct analogs with the above experimental and theoretical approaches hardly can be realized. Really, it is rather very difficult to discover and identify some solid precipitates in a nanosized droplet. As for CALPHAD, in most cases it would be rather very incorrect to interpret some internal subnanosized inclusions in a nanodroplet as thermodynamic phases (see also review [18] by Rusanov). Presumably, just for this reason, in the available papers on NANOCALPHAD, a different meaning is included into the notion of the phase diagram in comparison with that in the bulk CALPHAD and in our above MD approach which seems, however, to be much closer in methodology to the conventional interpretation of the bulk phase diagram. Really, when NANOCALPHAD is employed, including applications to Au-Si nanoalloys, equilibrium between two nanosized objects or equilibrium between NP (or nanodroplet) and a bulk body is considered. For example in [3] the next pairs of objects are treated proposing equilibrium between them: (i) solid NP – nanodroplet; (ii) nanowire – liquid nanodroplet; (iii) solid macrophase – bulk liquid phase; (iv) solid macrophase – liquid nanodroplet. The last of the above systems seems to be rather sophisticated as it assumes equilibrium between an Au-Si nanodroplet of the spherical shape and the bulk Si or Au. Really, in such systems the spreading phenomenon can take place and, respectively, it is not clear a priori that the complete wetting will not transform the droplet into a 2D wetting layer. For this reason in the present paper we have considered cases (i)-(iii) only. The first system, i.e. “spherical solid diamond Si or fcc Au NP – Au-Si nanodroplet of the same radius” is of interest as in [2-4] just for this system some contradictory results are reported. As for the second case, it is also of special interest as such a system is used in the well-known and promising technology of growing Si nanowhiskers by the vapor-liquid-solid method [6, 19]. Obviously, the process of the whisker growing should be realized at a temperature a bit higher than $T_e$ i.e. in the vicinity of the eutectic point of the nanosystem. Otherwise precipitation of some solid Si inclusions can occur in the Au-Si droplet instead of regular atom by atom precipitation on the whisker butt.

In general, our thermodynamic simulation results for the “spherical solid diamond Si or fcc Au NP – Au-Si nanodroplet” system are consistent with our MD results (figure 3): in comparison with the macroscopic phase diagram [7], the eutectic temperature decreases by about 150 K, and the $x_e$ value slightly shifts toward a lower $x$ value. It should be noted, however, that the MD results are attributed to Au-Si NPs of radius $r = 2$ nm. The MD simulation of larger objects is problematic. At the same time, according to [3, 4], CALPHAD should not be applied, at least without taking into account the size dependence of the surface tension, to NPs of radius $r < 5$ nm. This determines the choice of the value of radius $r = 5$ nm for our thermodynamic calculations and for calculations dicussed in [2, 3]. In [4], particles of the same size range, but with a slightly larger radius of $r = 7$ nm, are considered. As it was noted above, the results of [2, 4] demonstrate an insignificant (not larger than by 10 K) decrease of $T_e$. Besides, in [3, 4] a small shift of $x_e$ to lower $x$ values was found. In [2] such a shift was not revealed at
all. So, our results for the system shown in figure 1a are most consistent with the NANOCALPHAD results [3] where the shift of $T_e$ is about 70 K.

It should also be noted that in [4], instead of equations (2) and (3) for $G_L^{(S)}$ and $G_S^{(S)}$ formulas

$$G_L^{(S)} = 3\sigma_L V_L/r, \quad G_S^{(S)} = 3\sigma_S V_S/r$$

(6)

were used where, following to G. Kaptay [1], the different numeric factor (“3” instead of “2”) was employed. On the one hand, the justification of formulas (6) in [1] is quite reasonable (see also [4]). On the other hand, the right-hand sides of equations (2) and (3) correspond to the product of the molar volume and the capillary pressure, which is also quite adequately justified in a number of monographs, including [14]. Following to [1], for the nanosystem shown in figure 1b the next equations should be written instead of (4):

$$G_L^{(S)} = 3\sigma_L V_L/r, \quad G_S^{(S)} = 2\sigma_S V_S/r.$$  

(7)

However, when equations (7) are employed instead of (4), the phase diagram (curve 4 in figure 5) demonstrates a very high, i.e. inadequate value of the eutectic temperature of about 850 K. Besides, if the curve 4 in figure 5 is extrapolated to $x \to 0$, the temperature of liquidus will tend to a very high value exceeding 2000 K which is much higher than the bulk melting temperature of Au (1336 K). Accordingly, at the moment, we have not decided to employ equations (6) instead of (4).

For the system presented in figure 1b, i.e. for the Si nanowhisker with the Au-Si nanodroplet on its butt, the thermodynamic simulation (curve 3 on figure 5) predicts a shift of the bulk liquidus line towards higher liquidus temperatures including the increase of the eutectic temperature by about 100 K that agrees with the results on the same system obtained in [3]. Obviously, the increase of $T_e$, instead of its depression for the system in figure 1a, relates to different numerical multipliers in equations (4) for $G_L^{(S)}$ and $G_S^{(S)}$. Curve 3 in figure 5 demonstrates also a significant growth of the limiting (at $x \to 0$) value of the liquidus temperature in comparison with the bulk phase diagram. An analogous result was obtained in [3]. We believe that it is an artefact of the thermodynamic simulation appearing at $x \to 0$. However, we have not yet a relevant explanation of such an artefact.

In our NANOCALPHAD simulations we did not take into account the interfacial solid-liquid terms into the excess (surface) Gibbs energies. On the one hand, we are not sure that the internal (interfacial) boundaries should affect the equalities of the chemical potentials in the contacting nanophases. On the other hand, the above surface terms $G_L^{(S)}$ and $G_S^{(S)}$ are presented by the excess (capillary) pressure multiplied by the molar volume. An analogous interfacial term would be negligibly small.

5. Conclusion

So, both atomistic and thermodynamic simulations indicate a change in the shape of the phase diagram during the transition from the bulk Au-Si alloy to binary nanosystems. In particular, thermodynamic simulation predicts a noticeable shift of the phase diagram towards lower temperatures (approximately by 150 K) and a slight shift of $x_e$ a lower molar fraction of Si in the case of the system presented in figure 1a. The atomistic simulation of nanoparticles with of radius $r = 2$ nm demonstrates a more noticeable decrease in the eutectic temperature (by 250 K) and a much more significant decrease of $x_e$ towards the value $x_e \approx 0.1$ instead of $x_e^{(s)} = 0.2$. At the same time, the points of the phase diagram obtained by the MD method are characterized by a large scattering, and the right branch of the MD phase diagram ($x > x_e$) differs much more noticeably from the bulk phase diagram than the diagram 2 in figure 5 obtained by using the thermodynamic simulation. For the system shown in figure 1b, i.e. for the Si nanowhisker with the Au-Si nanodroplet on its butt our thermodynamic simulation predicts not diminishing but noticeable growing the eutectic temperature in comparison with its bulk value. Our results agree with the NANOCALPHAD results [3] and seem to be quite relevant. At the same time, we have revealed a number of open problems worth to be solved in the future.
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