

Size Dependency of Melting Point of Crystalline Nano Particles and Nano Wires: A Thermodynamic Modeling

Eun-Ha Kim and Byeong-Joo Lee*

Department of Materials Science and Engineering,
Pohang University of Science and Technology,
San 31, Hyoja-dong, Nam-gu, Pohang-si, Gyeongbuk 790-784, Korea

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A semi-empirical thermodynamic model for size dependency of melting point of nano particles and wires has been proposed by introducing a size dependency of surface energy. The model predicts the size dependency of melting point of nano particles and wires for a wide range of elements: fcc (Au, Pt, Ni), hcp (Mg), and bcc (W), all in good agreement with experimental data and/or molecular dynamics simulations. Since the model is free from adjustable parameters, it is applicable to a wider range of materials.

Keywords: melting point, nano particle, nano wire, thermodynamic model, molecular dynamics

1. INTRODUCTION

Nano-structured materials have attracted a great deal of interest due to their unique properties and influence on next generation industry. With advances in technology, the size of devices and device materials is getting smaller, down to the nanometer scale. Various fundamental physical properties are expected to change as the material size decreases. A typical example of the size dependency of physical properties is the melting point depression, which was first theoretically predicted by Pawlow [1] and demonstrated by Takagi [2] by transmission electronic microscope observation. Because melting point is one of the basic thermodynamic properties, it is expected that the size effect would also affect other thermodynamic properties. This means that reference thermodynamic data for bulk materials accumulated for a long time may need modification in order to be applicable to nanomaterials science, and it is necessary to predict the melting point depression of nano materials accurately as a function of size.

The melting points of nano particles predicted by Pawlow were much higher than those in the experimental data [3]. Hence, several models [2,4–19] have been suggested in order to predict the size dependency of melting points more accurately. Some models are based on thermodynamic equilibrium among three phases, solid, liquid, and vapor; others are based on two phases, solid and liquid. Differences among

individual models are reviewed in detail by Borel [3]. The three-phase models [1,5,7] assume the formation of a liquid film on the solid surface (premelting), and determine the melting point from the equality of chemical potentials. These models are too complex and/or use model parameters of which values are hard to determine. Besides, these models cause a contradiction for solid particles of a few nanometers, predicting that the particles should be liquid instead of solid [20]. Recently, some models based on the two-phase equilibrium [4] but modified by introducing the size and/or temperature dependency of thermodynamic quantities were developed [16–19]. For example, Wang *et al.* [16] introduced a size dependency to the latent heat considering the formation of liquid film on the solid surface as was done in a three-phase equilibrium model [12]. Tanaka and coworkers [17–19] introduced a correction factor to the resultant melting point depression. These models predict the size dependent melting point successfully. However, the determination of size dependency of latent heat or the amount of correction factor in the above models is not predicative but needs a fitting to experimental data.

The purpose of present study is to propose a new method for prediction of the size dependency of melting point of nano particles and nano wires, without using fitting parameters. The present model is based on solid/liquid two-phase equilibrium, but introduces a size dependency to the surface energy. The model was built up to predict melting points of Au nano particles and was found to be in good agreement with experiments [6,7]. The model was then extended so that it could also predict the melting points of nano wires. The

*Corresponding author: calphad@postech.ac.kr
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extended model was applied to the prediction of melting points of nano particles and wires of a wide range of materials (fcc, hcp, and bcc metallic elements). Due to the lack of experimental information on the size dependency of melting points of nano particles and nano wires, a molecular dynamics (MD) simulation based on the modified embedded atom method (MEAM) potentials [22-24], which is known [25] to reproduce the melting point depression well, is carried out. Good agreement is obtained between the model prediction and the MD simulations for the melting point depression of nano particles and nano wires, and details of the method and results are reported in the present article.

2. MODELING

2.1. Basic formalism

For a small particle, the molar Gibbs free energy of melting can be described as

$$\Delta G_{particle}^{S \rightarrow L} = \Delta G_{bulk}^{S \rightarrow L} + \Delta G_{surface}^{S \rightarrow L} \quad (1)$$

Here, $\Delta G_{bulk}^{S \rightarrow L}$ is the Gibbs free energy of melting for bulk materials, which is often expressed as follows, assuming that enthalpy (ΔH_m) and entropy (ΔS_m) of fusion are constant near the melting point (T_m):

$$\Delta G_{bulk}^{S \rightarrow L} = \Delta H_m - T \cdot \Delta S_m = \Delta H_m - T \cdot \frac{\Delta H_m}{T_m} = \frac{\Delta H_m}{T_m} (T_m - T) \quad (2)$$

$\Delta G_{surface}^{S \rightarrow L}$ represents the surface effect known as the capillarity effect or the Gibbs-Thomson effect. For a spherical particle of radius r , the surface effect term is given by

$$\Delta G_{surface}^{S \rightarrow L} = \frac{2\gamma_L}{r} V_m^L - \frac{2\gamma_S}{r} V_m^S \quad (3)$$

where γ and V_m represent surface energy and molar volume of individual phases, respectively. The expression for the melting point depression is derived by setting $\Delta G_{particle}^{S \rightarrow L} = 0$ as follows:

$$T_m - T = \Delta T_m = \frac{T_m}{\Delta H_m} \cdot \frac{2}{r} (\gamma_S V_m^S - \gamma_L V_m^L) \quad (4)$$

The amount of melting point depression due to the capillarity effect can be predicted from Eq. 4 once the necessary physical quantities, enthalpy of fusion, surface energy, and molar volume of solid and liquid phases, are known. It should be mentioned here that all the physical quantities have temperature and size dependencies. However, the size dependencies are generally unknown. The size dependency of enthalpy of fusion has only been considered assuming the formation of liquid film on the solid surface and resultant decrease of solid portion [12], as will be introduced again later on. The temperature dependency of enthalpy of fusion is not known. Only incomplete information is available for the temperature dependency of surface energy and molar volume. Further, the values for liquid in an undercooled region are not generally known. In a situation for which all necessary physical quantities are not completely known, it would be meaningless or not helpful for accurate prediction to use size or temperature dependent expressions only for part of quantities.

The main concern of the present work is to predict the melting point depression most efficiently, that is, using a minimum amount of well available experimental information. The simplest approximation would be to use values from the literature measured at melting point or at room temperature for the physical quantities (see Table 1). The solid curve in Fig. 1 shows how Eq. 4 works when the melting point data are used for all physical quantities: surface energy, molar volume, and heat of fusion. Further assumption of equal molar volume for solid and liquid can be made based on the fact that those values approach each other with decreasing temperature from the melting point. The dashed curve in Fig. 1 was obtained by using the room temperature solid molar volume data (V_S) for solid and liquid instead of the the melting point data, V_m^S and V_m^L . In addition to the improvement obtained, the advantage of the second approximation is that the room temperature molar volume data of solid can be easily found in most works in the literature. However, both predictions (solid and dashed curves in Fig.

Table 1. Physical properties of elements necessary for the present thermodynamic prediction of melting point depression of nano particles and wires: T_m the melting point, $\tilde{\alpha}_s$ and $\tilde{\alpha}_l$ the surface energy of solid and liquid at T_m , $\tilde{\Delta H}_m$ the latent heat of melting, r_e the first nearest-neighbor distance, V_S the molar volume of solid at room temperature. V_m^S and V_m^L are molar volume of solid and liquid at T_m

Elements	T_m^a (K)	γ_s^b (J/m ²)	γ_l^b (J/m ²)	ΔH_m^a (kJ/mol)	r_e^c (nm)	V_S^d	V_m^{Se} (m ³ /mol, 10 ⁻⁶)	V_m^{Le}
Au	1337	1.333	1.130	12.55	0.288	10.20	10.7	11.4
Pt	2042	2.203	1.866	22.18	0.277	9.09	-	-
Ni	1728	2.080	1.780	17.50	0.249	6.59	-	-
W	3695	2.765	2.343	35.20 ^f	0.274	9.47	-	-
Mg	923	0.688	0.566	8.48	0.320	14.00	-	-
Sn	505	0.661	0.560	7.03	0.281	16.29	-	-

^areference 26. ^breference 27. ^creference 28. ^dreference 29. ^ereference 6. ^fLiterature values for the latent heat of melting of W are divergent. In the present study, we used a value from references [29-31], instead of reference [26].

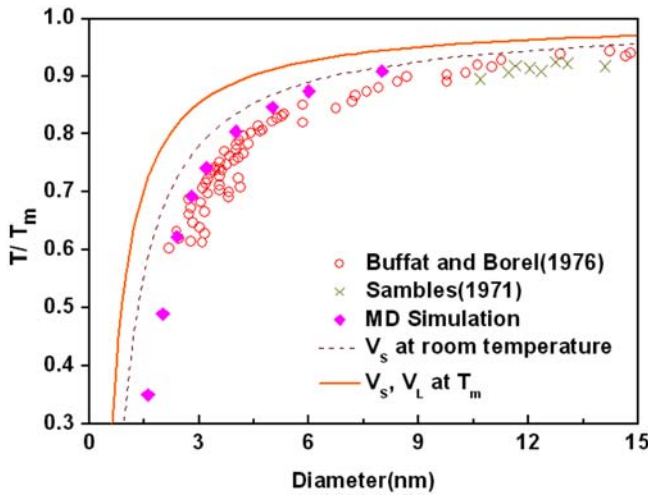


Fig. 1. Normalized melting temperature of Au particles as a function of diameter. Dotted and solid curves are thermodynamic predictions using Eq. 4 with different assumptions for molar volume. Symbols are from experiments [6,7] and the present MD simulation using an MEAM interatomic potential [22].

1) are still far from the experimental data and need further improvements. It should be noted here that the MD simulation using the MEAM interatomic potential [22] shows very good agreement with experiments and can be used for comparison with the thermodynamic approach later on for the cases in which experimental information is not available.

2.2. Review of previous models

The poor agreement between the thermodynamic approach and experiments shown in Fig. 1 is the reason why many modified versions of Eq. 4 have been proposed. Two modifications can be found in the recent literature. One is the introduction of size dependency to the enthalpy of fusion [12]. This idea originates from the concept of surface pre-melting, which means that the atoms in the surface region can be regarded as liquid atoms. Because the solid (core region) portion decreases with decreasing particle size, the amount of heat of fusion should also decrease with decreasing size according to this idea. Indeed, the size dependency of heat of fusion was experimentally confirmed by Lai *et al.* [12], who measured the heat of fusion of Sn nano particles of various sizes, proposed a mathematical expression for the effect's size dependency, and predicted the melting point depression in good agreement with experimental data. This expression has been also applied successfully to the predictions for Zn nanowires [16]. However, the expression for the size dependency of heat of fusion involves a model parameter which can only be determined by fitting to experimental data, which is generally unavailable. The other approach is to introduce a correction factor to Eq. 4 [17-19]. The introduction of a correction factor originates from the energy dif-

ferences among edges, vertices, and faces on solid surfaces. Actually, a size dependency had to be introduced because the relative portions of edges, vertices, and faces changes with particle size. However, because of the difficulty in defining the energy of individual components (edges, vertices, and faces) and the change of their portions, a simple (constant) correction factor is used. The value of the correction factor is determined by fitting to experimental data on melting point depression. This method works only for relatively large particles ($r > 5$ nm), probably because of the lack of size dependency of the correction factor. The recent work by the same authors [19] strongly indicates that a size dependency of solid surface energy should be introduced.

The above review of previous works shows that the size dependency of thermodynamic quantities should be introduced for successful prediction of the melting point depression for small particles ($r < 5$ nm). In order to examine the size dependency of thermodynamic properties that would yield a good agreement with experiments, Eq. 4 is rearranged as follows, with the further simplification of equal molar volume for solid and liquid:

$$r \frac{\Delta T_m}{T_m} = \frac{2(\gamma_s - \gamma_L)V_s}{\Delta H_m} \quad (5)$$

Then, the experimental data and the MD simulation results for the melting point of Au nano particles are plotted in the form of the left hand side of Eq. 5, $r \cdot \Delta T_m/T_m$, as shown in Fig. 2. Both experimental and MD simulation data points clearly show an increase with decreasing size, which means that the right hand side of Eq. 5 should increase with decreasing particle size. From this point of view, the introduction of size dependency for heat of fusion [12,16] can be regarded as a desired change, while introduction of the constant correction factor [17-19] is not enough.

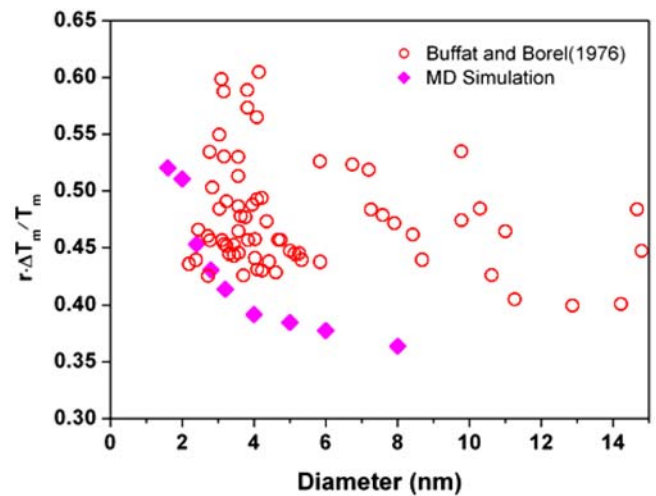


Fig. 2. Melting point depression of Au nano particles in the form of $r \cdot \Delta T_m/T_m$. Unfilled and filled symbols are from experiment [7] and MD simulation, respectively.

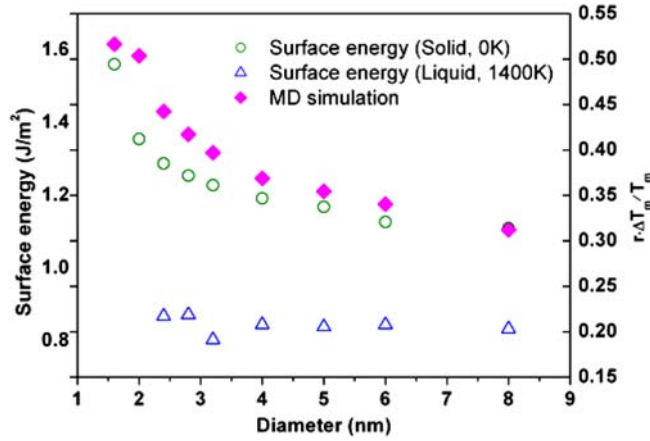


Fig. 3. Size dependency of surface energy of solid (0 K) and liquid (1400 K) Au nano particles by an atomistic calculation. MD simulation results for the melting point depression of Au nano particles are also presented in the form of $r \cdot \Delta T_m / T_m$ for comparison.

2.3. Building up of a new model

In the present study, it was decided to pay attention to the size dependency of surface energy because of the difficulty in predicting the size dependency of heat of fusion. For this, the surface energy of solid and liquid Au particles of various sizes was calculated by an atomistic calculation. As shown in Fig. 3, the surface energy of solid particles increases with decreasing size while that of liquid particles remains unchanged. The similar size dependency between the solid surface energy γ_s (or the surface energy difference between solid and liquid ($\Delta\gamma = \gamma_s - \gamma_L$)) and the MD simulation results implies that the introduction of a size dependency to γ_s (or $\Delta\gamma$) may be a reasonable and desired approach. Now the issue is to find a mathematical expression that can represent the size dependency of γ_s (or $\Delta\gamma$) without importing an additional model parameter.

Note that the origin of surface energy is often sought in the existence of broken bonds on surfaces. In Fig. 4, atomic configurations on a flat surface and on a convex surface are illustrated schematically. Here, filled spheres represent surface atoms and empty spheres represent missed atoms on the upper layer due to the existence of the surface. The flat surface can be regarded as the surface of a bulk material while the convex surface is that of a particle with a size (radius) of r . One can see that the number of missed atoms for each surface atom changes depending on the curvature of the surface. The number of broken bonds for each surface atom increases as the radius of particle decreases. Therefore, once the surface energy is assumed to be proportional to the number of broken bonds per surface atom, an increase of surface energy can be expected with a decrease of particle size. This is the desired size dependency for the surface energy.

The increase of surface energy of a spherical particle compared to its bulk can be estimated by the increase of the num-

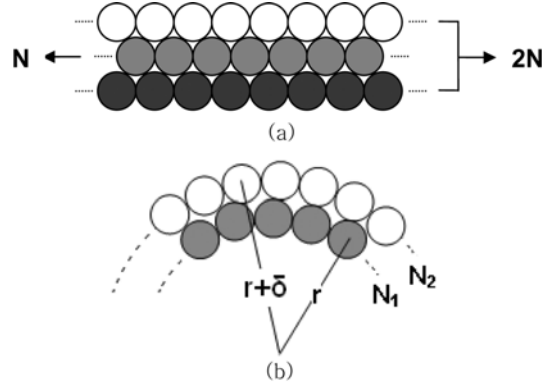


Fig. 4. Atomic configurations on a flat surface and on a convex surface.

ber of broken bonds per surface atom or the number of missed atoms on the upper layer of the surface. The number of missed atoms on the upper layer of the surface is proportional to the area of the upper layer. In the case of the bulk surface (Fig. 4(a)), the area of the upper layer is the same as that of the surface. However, in the case of a spherical particle with a radius r (Fig. 4(b)), the area of the upper layer is larger than that of the surface layer, and the ratio can be expressed as follows:

$$\frac{A_{\text{upper layer}}}{A_{\text{surface}}} = \frac{(r + \delta)^2}{r^2} = \left(1 + \frac{\delta}{r}\right)^2 \quad (6)$$

Here, δ is the interlayer distance between the two surface layers. The solid surface energy can now be expressed in a functional form of the particle size r by multiplying Eq. 6. The following is the resultant expression for the melting point depression, obtained when considering the size dependency of the solid surface energy:

$$\Delta T_m = \frac{2V_s T_m}{r \Delta H_m} \left[\gamma_s \left(1 + \frac{\delta}{r}\right)^2 - \gamma_L \right] \quad (7)$$

Now the final issue is how to estimate the interlayer distance δ in Eq. 7. Since the interlayer distance depends on the crystallographic orientation of surfaces, an effective value has to be derived by some means. The interlayer distance must be equal to or smaller than, but proportional to, the first nearest-neighbor distance r_c for crystalline materials. The simplest approximation, without introducing any new adjustable parameter, is to take r_c as the effective average interlayer distance on surfaces. However, r_c is clearly an overestimation of the average interlayer distance on surfaces. Indeed, it was confirmed during the present study that the above approximation overestimates the melting point depression. A great effort was made to find an adequate expression for the melting point depression, taking the size dependency term, Eq. 6, into consideration. The final expression found to reproduce the experimental

and MD simulated melting depression of Au nano particles was to multiply the factor of Eq. 6 by the solid/liquid surface energy difference $\Delta\gamma = (\gamma_s - \gamma_l)$, substituting r_e for δ as follows:

$$\Delta T_m = \frac{2V_s T_m}{r \Delta H_m} \Delta\gamma \left(1 + \frac{r_e}{r}\right)^2 \quad (8)$$

3. RESULTS AND DISCUSSION

3.1. Comparison with experimental data

The reliability of Eq. 8 can now be evaluated by comparing the predicted melting point depression of Au nano particles with the experimental data. Such a comparison is made in Fig. 5(a), in which MD simulation and the prediction made without considering the size dependency of surface energy are also presented. It is shown that the new prediction, Eq. 8, gives a good agreement with experiments and MD simulation, and a great improvement is made by introducing the size dependency of surface energy. Such a good

agreement as that shown in Fig. 5(a) may not be surprising since the final mathematical expression, Eq. 8, was determined to reproduce the experimental and MD simulated melting depression of Au nano particles, as mentioned earlier. Similar comparison is made for Sn nano particles in Fig. 5(b), and the satisfactory agreement between the prediction and experimental data makes the final expression a convincing one.

3.2. Extension for nano wires

The present model for the melting point depression of nano particles can easily be modified into a suitable form for nano wires. It should be noted here that for wires the capillarity effect term is given by $\gamma V/r$ instead of $2\gamma V/r$ in Eq. 3, and the surface area is proportional to r instead of r^2 in Eq. 6. Based on these, and by a similar procedure, the expression for the melting point depression of nano wires can be derived as follows:

$$\Delta T_m = \frac{1}{r} \frac{V_s T_m}{\Delta H_m} \Delta\gamma \left(1 + \frac{r_e}{r}\right) \quad (9)$$

The predicted melting points of Au nanowires using Eq. 9 are presented in Fig. 6 in comparison with MD simulations. For a given diameter, there can be several different nano wires depending on the crystallographic orientation along the longitudinal directions. The MD simulations were carried out for three different nano wires with [100], [110], and [111] orientations. In Fig. 6, it is shown that the melting point of nano wires is dependent on the crystallographic orientation of the wires. Among the three nano wires studied, the melting point of the [110] wire is highest and closest to the present prediction. It is believed that the side wall surfaces of [110] nano wires have the lowest energy on average and are most resistant to melting.

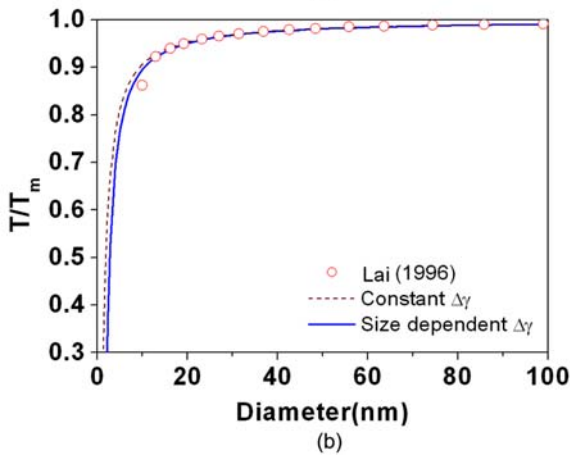
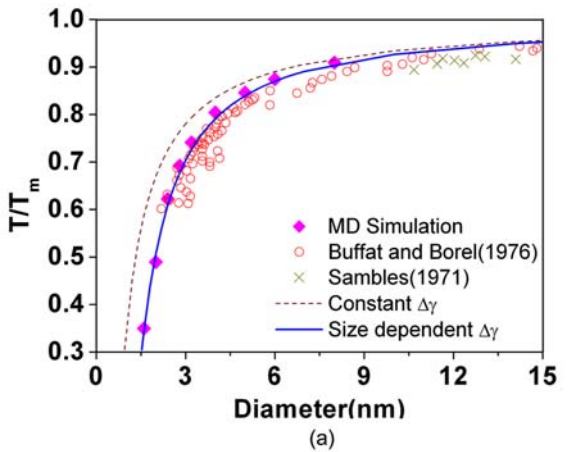


Fig. 5. Normalized melting temperature of (a) Au and (b) Sn nano particles, as a function of diameter. Curves represent the present prediction with (solid curve) and without (dotted curve) size dependency of surface energy. Symbols are by experiments or MD simulation.

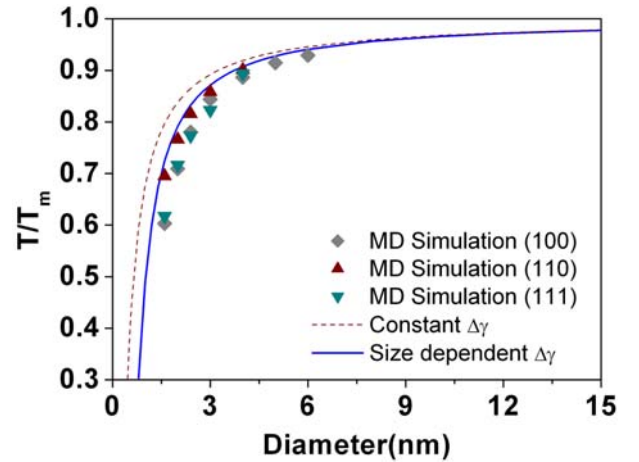


Fig. 6. Normalized melting temperature of Au nano wires, as a function of diameter. Curves represent the present prediction with (solid curve) and without (dotted curve) size dependency of surface energy. Symbols are by MD simulations.

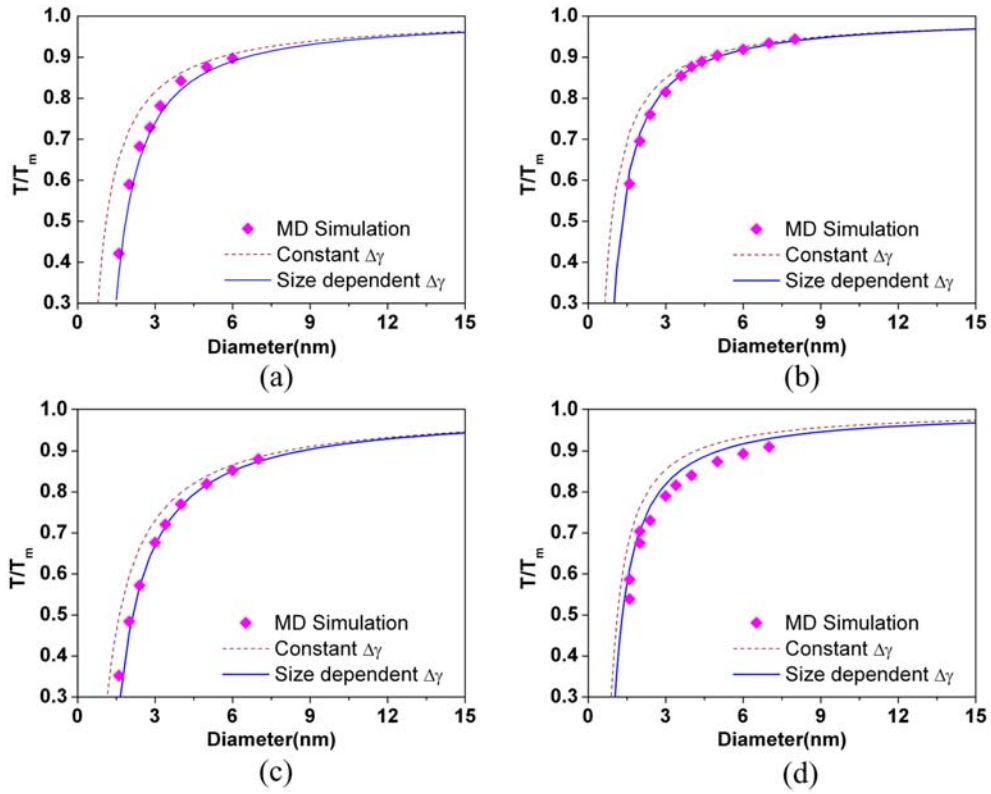


Fig. 7. Normalized melting temperature of (a) Pt, (b) Ni, (c) Mg and (d) W nano particles, as a function of diameter. Curves represent the present prediction with (solid curve) and without (dotted curve) size dependency of surface energy. Symbols are by MD simulation.

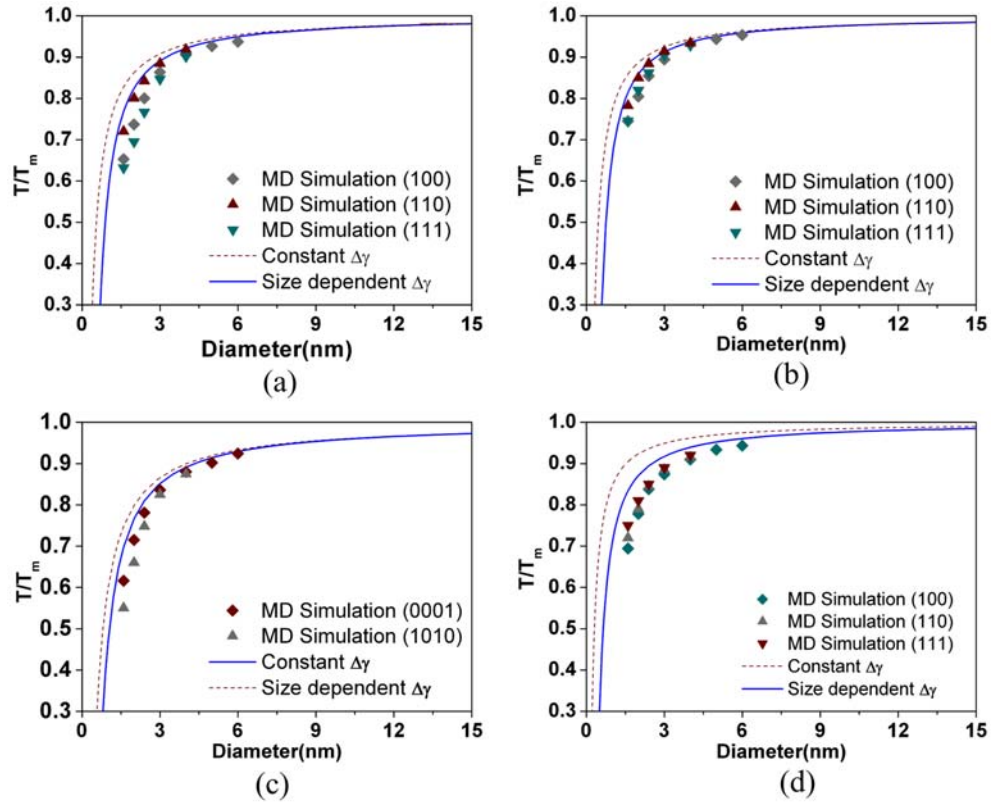


Fig. 8. Normalized melting temperature of (a) Pt, (b) Ni, (c) Mg and (d) W nano particles, as a function of diameter. Curves represent the present prediction with (solid curve) and without (dotted curve) size dependency of surface energy. Symbols are by MD simulation.

3.3. Application to a wider range of elements

It has been shown that the new model, Eqs. 8 and 9, for the melting point depression of nano particles and wires yields a good agreement with experimental or MD simulation data for Au and Sn. However, since the modification from Eq. 7 to Eq. 8 and hence to Eq. 9 is made in an *ad hoc* manner, equation applicability needs to be further verified for a wider range of materials. In the present work, Eqs. 8 and 9 were further applied to other fcc elements (Pt, Ni) with different values of r_c , and elements (Mg, W) with different crystal structures. As no experimental data is available for the size dependency of melting points of those elements, MD simulations were carried out again for comparison.

The size dependency of melting points for nano particles and wires of the above elements (Ni, Pt, Mg, W) predicted by the present model using the physical constants listed in Table 1 is presented in Figs. 7 and 8, respectively. Even though the derivation of Eqs. 8 and 9 can only be semi-empirical, it is shown that these models can predict melting points of nano particles and wires of a wide range of elements reasonably well.

4. CONCLUSION

A new semi-empirical thermodynamic model for prediction of melting point depression of nano particles and wires as a function of size has been proposed. By introducing a size dependency to the surface energy, which was found by an atomistic calculation, a great improvement is obtained in the accuracy of prediction for a wide range of metallic elements. This model is free from adjustable parameters and is further applicable to a wider range of materials.

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