Size-Dependent Vacancy Concentration in Nickel, Copper, Gold, and Platinum Nanoparticles

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ABSTRACT: Size-dependent thermodynamic model is presented to simultaneously analyze stress and vacancy concentration, along with their coupling behavior in spherical metal nanoparticles. A nanoparticle is treated as a composite with a core lattice and a surface shell, which both have their corresponding thermodynamic properties. Thermodynamic analysis of Ni, Cu, Au, and Pt particles shows that the vacancy concentration in the core and the surface shell could be significantly decreased for smaller particles. The apparent vacancy concentration in the whole nanoparticle reaches the maximum at the critical particle size of about 100 nm and is lower for larger or smaller particles. This result provides comprehensive understanding of the vacancy concentration in nanomaterials, which had been represented by two opposite views in the past decades.

1. INTRODUCTION

Nanosized and nanostructured materials possess many unique properties, which differ from their bulk counterparts due to the high surface-to-volume ratio. In nanomaterials and nanoporous materials, in particular, the surface-to-volume ratio is extremely large, which makes surface stress contributions quite substantial for both physical14–20 and chemical21–25 properties. Recent research26–29 showed that both vacancy formation energy and concentration change significantly with the material size, especially at the nanometer scale.

The vacancy defects in metallic nanoparticles play an important role in many physical–chemical properties, including mechanical, optical and electrical properties, along with catalytic activity.14–20 Although the role of thermal vacancies in nanomaterials is vital for understanding these properties and related behavior, it has been quite difficult to investigate vacancies experimentally until now. In recent decades, positron annihilation spectroscopy has been used to study intrinsic defects in nanostructured materials.21–24 However, vacancy concentration measured by positron annihilation can be strongly influenced by experimental conditions.

Theoretically, many researchers have attempted to investigate the size-dependent vacancy formation energy in nanomaterials to understand the underlying physical mechanisms. Since the vacancy formation process involves breaking up atomic bonds, it was thought that the vacancy formation energy could be related to the crystal cohesive properties.30–33 Qi and Wang gave the relationship between the vacancy formation energy and the cohesive energy of small particles by considering the change of the atomic radius induced by the surface stress.30 They found that the vacancy formation energy depends on the lattice strain and that the vacancy formation energy is lower than in the corresponding bulk metals.30–33 Ouyang et al. theoretically predicted that the vacancy formation energy decreases with decreasing particle size and that the vacancy formation energy on the surface and at the interface is smaller than in the interior core.32–34 Gladkikh et al. proposed analogous idea that cohesive energy and melting temperature have similar dependence on particle size.35 They calculated the size-dependent vacancy formation energy in nanomaterials using proportionality between the vacancy formation energy and the melting temperature, concluding that the vacancy formation energy is reduced in smaller particles.35,36 Guisbiers et al. developed a theoretical model to account for the size-dependent vacancy formation energy and entropy based on the universal equation, in which they found that the vacancy concentration increases with decreasing sample size and increasing temperature.37,38 However, Müller et al. simulated an opposite result where the surface energy and surface stress contributions in metallic nanoparticles can actually increase the vacancy formation energy as the system size decreases.39 They also reported that the vacancy concentration decreased in the crystal core with smaller particle size.40 Recently, Salis et al. approximated surface stress as a constant.41 Total vacancy concentration has maximum at a critical particle radius due to the surface energy, which increases both the core and surface vacancy formation energy. However, the surface-to-volume ratio increases the relative concentration of surface defects for smaller particle size.

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Although nanoparticles can have various morphology due to different preparation methods, in the present theoretical work, we discuss spherical metal nanoparticles as an example. A nanoparticle is treated as a composite with a core lattice and a surface shell to study the size-dependent concentration of thermal vacancies in nanomaterials. In this paper, thermodynamic model is established by considering the surface energy and surface stress effects on the Gibbs free energy of vacancy formation. An accurate solution of size-dependent vacancy concentration containing the eigen parameters is provided, including biaxial surface eigenstress and biaxial Young’s moduli of the core and the surface. Surface stress, vacancy concentration, and their coupling behavior in surface shell and the core lattice are analyzed.

2. ANALYSIS

2.1. Deformation and Surface Stress of Nanoparticles. Usually, there are three common approaches to study the properties of surfaces: the sharp surface approach, the diffusive surface approach, and the interphase approach. Both diffusive surface and interphase approaches treat surfaces as three-dimensional (3D) objects. In the sharp surface approach, a single dividing interface of zero thickness is used to separate a dimensional (3D) objects. In the sharp surface approach, a single dividing interface of zero thickness is used to separate a dimensional (3D) objects. In the sharp surface approach, a single dividing interface of zero thickness is used to separate a dimensional (3D) objects. In the sharp surface approach, a single dividing interface of zero thickness is used to separate a dimensional (3D) objects.

The present study focuses on the fundamental elastic properties of a solid surface and considers an isotropic nanoparticle to simplify the theoretical analysis. A nanoparticle is modeled to be a spherical composite of a core and a surface shell coherently bonded to the core. In general, various defects may be introduced in nanoparticles during fabrication. In the present study, we consider only the core and the surface shell, surface eigenstress and stresses induced by vacancy concentration in the core and the shell, meaning that other defects are not analyzed here for simplicity. Furthermore, the core and the surface shell are assumed to be both mechanically isotropic. Since vacancies randomly appear in materials, it was assumed that the vacancies are uniformly distributed in the nanoparticles. Without deformation and any defects, the core has an original radius \( R_0 \) and the original thickness of the surface shell is denoted by \( \Omega_0 \).

When a nanoparticle is formed, its volume will change due to surface stress and/or all the defects. In this case, it is convenient to take the stress-free and defect-free nanoparticle as a reference. The total potential energy of a nanoparticle is given by

\[
U(\varepsilon) = V\mu(\varepsilon) + V\kappa(\varepsilon)
\]

(1)

Here, \( \varepsilon \) denotes strain, \( \mu \) is the surface energy density, \( \kappa \) is the core energy density, while \( V\mu \) and \( V\kappa \) is the surface and core volume of the nanoparticle, respectively.

For a nanoparticle with an original radius \( R_0 \) and the original thickness of the surface shell \( \Omega_0 \), the energy density is given by

\[
u(\varepsilon) = \nu(0) + 2 \times \left( \frac{\nu(0)}{2} \varepsilon \right) + \frac{1}{2} Y \varepsilon^2
\]

(2a)

\[
u(\varepsilon) = \nu(0) + \frac{1}{2} K\varepsilon^2 = \nu(0) + \frac{1}{2} K(3\varepsilon)^2
\]

(2b)

where \( \nu(0) \) and \( \nu(\varepsilon) \) are the generalized surface and core energy densities in the strain-free state, respectively; \( \nu(\varepsilon) \) is the eigenstress in the surfaces shell and \( \Omega \) is the surface biaxial Young’s moduli, while \( K\varepsilon^2 \) is the bulk modulus of the core; \( \varepsilon \) is the biaxial strain, and \( \varepsilon = 3\varepsilon \) is the volumetric strain.

Substituting eqs 2a and 2b into eq 1, the total potential energy of a nanoparticle is given by

\[
U(\varepsilon) = 4\pi R_0^2 \Omega(\nu(0) + 2\sigma_0 \varepsilon + 3R_0^2 K\varepsilon^2) + \frac{4\pi R_0^3}{3} \left( \frac{\nu(0)}{2} + \frac{9}{2} K_0^2 \varepsilon^2 \right)
\]

(3)

where \( \nu(0) \) is the generalized surface energy volume, \( \Omega(0) \) is the generalized core energy volume, \( \varepsilon = 3\varepsilon \) is the volumetric strain.

From eq 4, the initial strain in the core induced by the surface stress is given by

\[
e_0 = - \frac{2\sigma_0 \Omega_0}{2\Omega_0 + 3R_0 K_0}
\]

(5)

The biaxial surface and lattice stress of the nanoparticle are then, respectively given by

\[
\sigma = \sigma_0 + 3Y \Omega_0 / (3R_0 K_0)
\]

(6a)

\[
\sigma = 3K_0 \Omega_0 / (2Y + 3R_0 K_0)
\]

(6b)

Here, we consider that the nanoparticle consists of pure components, which have only vacancy defects. At a relatively small number of vacancies the crystal can be regarded as an ideal solid solution. At constant temperature, the solid solution sample volume can expressed as a function of stress and composition. For a given number of moles of the solvent in an ideal solid solution, its volume is a function of the number of vacancies, \( n_{cv} \), and the hydrostatic stress, \( \sigma \), at constant temperature. In differential form, one has:

\[
dV = \left( \frac{\partial V}{\partial n_{cv}} \right)_\sigma d\sigma + \left( \frac{\partial V}{\partial n_{cv}} \right)_\sigma d\sigma
\]

(7a)

The vacancy formation volume can be defined as

\[
\Delta V_v = \left( \frac{\partial V}{\partial n_{cv}} \right)_\sigma
\]

(7b)

Hooke’s law states that \( \sigma = K_0 \varepsilon \) is \( K_0 \varepsilon \) with \( K_0 \) being the isothermal vacancy-related bulk modulus. Thus, one has

\[
\Delta V_v = K_0 \varepsilon
\]
\[
\frac{\partial V}{\partial r} = \frac{V_0}{K_{r,v}} \]

(7c)

We assume the formation volume of a vacancy to be constant and independent of the number of vacancies and hydrostatic stress. Then, integrating eq 7a leads to the change in volume caused by vacancies and hydrostatic stress

\[
\Delta V \approx \bar{V}_{c,v} n_{sv} + \frac{V_0}{K_{r,v}} \sigma.
\]

(7d)

Dividing the core lattice volume change by the original core lattice volume gives

\[
\frac{\Delta a}{a_0} = \frac{1}{3} \left[ \frac{\bar{V}_{c,v}}{V_0} n_{sv} + \frac{\sigma}{K_{r,v}} \right].
\]

(8)

Similarly, we may introduce the formation volume of a vacancy, \( \bar{V}_{sv} \), inside the surface shell. The vacancy-induced volumetric change at stress-free condition is given by

\[
\Delta V_{sv} = \bar{V}_{sv} n_{sv}.
\]

(9)

Here, \( n_{sv} \) is the vacancy number inside the shell. Because the thickness of the surface shell is small, we may assume that the stress field with zero radial stress is homogeneously distributed there. With a vacancy defect, we have the elastic surface area strain, \( \Delta A_{sv,c} \), from linear elasticity

\[
\frac{\Delta A_{sv,c}}{A_0} = \frac{2}{3} \frac{\Delta \sigma}{\bar{V}_{sv}}
\]

(10a)

\[
\frac{\Delta \Omega_{sv}}{\Omega_0} = -\frac{2}{3} \frac{\Delta \sigma}{\bar{V}_{sv}}
\]

(10b)

where \( \Delta \sigma = \sigma - \sigma_0 \) is the change in surface tangential stress, with \( \sigma_0 \) being the surface eigenstress.\(^{43} \bar{V}_{sv} = V_{sv}/(1 - v_{sv}) \) is the surface vacancy-related biaxial Young’s modulus, and \( v_{sv} \) are the surface vacancy-related Young’s modulus and Poisson’s ratio, respectively. The total volume change of the surface shell induced by the stress and vacancies can be separated into the normal and tangential components as

\[
\frac{1}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} + \Delta \Omega_{sv} = \frac{1}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} - \frac{2}{3} \frac{\bar{V}_{sv}}{V_0} \frac{\Delta \sigma}{\bar{V}_{sv}}
\]

(11a)

In the interphase approach, the surface shell is coherently bonded with the core. Thus, the surface area strain should be equal to twice the linear strain of the core, i.e.,

\[
\frac{2}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} + \frac{2}{3} \frac{\Delta a}{a_0} = 2 \frac{\Delta a}{a_0}, \text{ or }
\]

\[
\Delta \sigma = \bar{V}_{sv} \left( \frac{\Delta a}{a_0} - \frac{1}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} \right)
\]

(12a)

On the other hand, eq 8 gives

\[
\sigma = K_{r,v} \left( \frac{\Delta a}{a_0} - \frac{\bar{V}_{c,v}}{V_0} n_{sv} \right)
\]

(12b)

The force balance requires\(^{44,45}\)

\[
\sigma R_{sv} + 2 \sigma_0 \Omega_0 = \sigma R_{sv} + 2 \Delta \sigma + 2 \sigma_0 \Omega_0 = 0 \quad (13a)
\]

Equation 13a is an explicit form of the so-called generalized capillary equation.\(^{46} \) Substituting eqs 12a and 12b into eq 11a yields

\[
K_{r,v} \left( \frac{\Delta a}{a_0} - \frac{\bar{V}_{c,v}}{V_0} n_{sv} \right) R_{0,s} + 2 \bar{Y}_{sv} \left( \frac{\Delta a}{a_0} - \frac{1}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} \right) \Omega_0
\]

\[+ 2 \sigma_0 \Omega_0 = 0 \quad (13b)\]

eq 13b gives the solution of

\[
\frac{\Delta a}{a_0} = \frac{2 \sigma_0 \Omega_0}{\bar{Y}_{sv}/(K_{r,v} R_{0,s})}
\]

(14a)

\[
\Psi = 3 + 2 \bar{Y}_{sv} \Omega_0 / (K_{r,v} R_{0,s})
\]

(14b)

eq (14) shows that the change in lattice constant depends on the vacancy concentration inside the core lattice and the surface shell, along with the particle size. Once the lattice strain is known, the lattice stress and the surface stress are calculated from eq 12a and eq 12b, respectively, yielding

\[
\sigma = -2 \frac{\Omega_0}{R_{sv}} \Theta
\]

(15a)

\[
\sigma = \frac{\Psi}{\Omega_0}
\]

(15b)

\[
\Theta = 3 \sigma_0 \Omega_0 + \bar{Y}_{sv} \left( \frac{\bar{V}_{c,v}}{V_0} n_{sv} - \frac{\bar{V}_{sv}}{V_0} n_{sv} \right)
\]

(15c)

Here, \( \Theta \) is the stress parameter. The sample strain is given by

\[
\frac{\Delta l}{l_o} = \frac{\Delta a}{a_0} \left( 1 - \frac{\Omega_0}{R_{sv}} \right) + \left( \frac{1}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} - \frac{2}{3} \frac{\bar{V}_{sv}}{V_0} \frac{\Delta \sigma}{\bar{V}_{sv}} \right) \Omega_0
\]

\[+ \frac{1}{3} \frac{\bar{V}_{sv}}{V_0} n_{sv} \frac{\Delta a}{a_0} - \frac{2}{3} \frac{\bar{V}_{sv}}{V_0} \frac{\Delta \sigma}{\bar{V}_{sv}}
\]

\[= \frac{2 \sigma_0 \Omega_0}{\bar{Y}_{sv}/(K_{r,v} R_{0,s}) + \bar{Y}_{sv} (\bar{V}_{c,v}/V_0 n_{sv} - \bar{V}_{sv}/V_0 n_{sv})} \Omega_0
\]

(16)

Equation 16 describes the relationship between the sample strain and the lattice strain, showing that the changes in sample dimensions stem from the interdependent contributions of the surface and lattice core. For vacancy-free nanoparticle, the lattice strain calculated by eq 14 is simplified to eq 5. Then the lattice stress and the surface stress calculated from eq 15 is simplified to eq 6.

2.2. Vacancy Concentration in Nanoparticles. For investigating the vacancy concentration in nanoparticles, it is helpful to start from the definition of vacancy formation in bulk materials. For a large enough system \((N > 10^3 \) atoms\), which consists of \(N\) atoms and \(n\) vacancies, according to the general definition of the chemical potential, the chemical potential of vacancies is determined as

\[
\mu_{\nu}^{(a)} = \frac{\partial \Delta G}{\partial n} = \Delta H_f - T \Delta S_f + k_B T \ln \frac{n}{N + n}
\]

(17)
The standard chemical potential of the vacancies is determined as the infinite crystal free energy change per 1 added vacancy, disregarding the mixing entropy:

$$\mu_V^{(0)} = \Delta H_\nu - T \Delta S_j$$

(18)

And consequently

$$\mu_V^{(s)} = \mu_V^{(0)} + k_B T \ln \frac{n}{N + n} = \mu_V^{(0)} + k_B T \ln X_v$$

(19)

It is taken into account here that if \( n \) is a small quantity, the concentration of vacancies is

$$X_v \approx n/(N + n)$$

(20)

The free energy of the crystal containing \( n \) vacancies can be represented in the form of a sum

$$G = \sum_i N \mu_i + n \mu_V^{(0)}$$

(21)

Here, \( N_i \) and \( \mu_i \) are the number of atoms of type \( i \) and their chemical potential, respectively. Consequently, the change of \( n \) may lead to equilibrium

$$\mu_V^{(s)} = \frac{\partial \Delta G}{\partial n} = 0$$

(22)

i.e., the equilibrium concentration of the vacancy differs from zero and is equal to

$$X_v^0 = \exp \left( - \frac{\mu_V^{(0)}}{k_B T} \right) = \exp \left( - \frac{\Delta S_j}{k_B} \right) \exp \left( - \frac{\Delta H_\nu}{k_B T} \right)$$

(23)

\( \Delta S_j \) is the vacancy formation entropy, which is very small, so we ignore it in the analysis. For our model, in nanoparticle systems, based on the Gibbs-based 3D model, the chemical potential of vacancy in the surface shell equals to the chemical potential of vacancy in the core. In the following, we determine the vacancy concentration inside the surface shell by utilizing equal vacancy chemical potentials.

The chemical potentials of vacancies at constant temperature in the core and the surface shell are respectively given by

$$\mu = \mu^0 + k_B T \ln X_c - \sigma V_{c,v}$$

(24a)

$$\mu = \mu^0 + k_B T \ln X_s - 2 \sigma V_{s,v}/3$$

(24b)

Here, \( k_B \) is the Boltzman’s constant, \( T \) is the absolute temperature, \( X_c \) and \( X_s \) denote the concentration of vacancies inside the core and the shell, respectively, with \( \mu^0 \) and \( \mu^0 \) being the corresponding reference chemical potentials. Equation 24 indicates that the vacancy concentrations and stresses in the core and the shell play an important role in the chemical potentials. On the basis of the equal vacancy chemical potential in the core and the surface shell, we have, from eqs 24a and 24b:

$$X_v^{sp} = X_v^{sp} \exp \left( - \frac{\Delta \mu^0 - \sigma V_{c,v} + 2 \sigma V_{s,v}/3}{k_B T} \right)$$

(25a)

with \( \Delta \mu^0 = (\mu^0 - \mu^0) \). Eq 15a indicates that \( \sigma \to 0 \) when the ratio of \( \Omega_b/R_0 \) approaches zero, which is satisfied in bulk materials. For this extreme case, eq 25a is reduced to

$$X_v^{sp} = X_v^{sp} \exp \left( \frac{\Delta \mu^0 - \sigma V_{c,v} + 2 \sigma V_{s,v}/3}{k_B T} \right)$$

(25b)

where the superscript “bp” denotes “big particle”. Eq 25b gives the expression of the surface vacancy concentrations in big particles, showing that the surface vacancies could be affected by the surface stress. As stated in the McLean adsorption isotherm, the reference chemical potential \( \mu^0 \) in the surface must be much lower than \( \mu^0 \) to cause higher vacancy concentration in the surface shell. It shows large gradients in vacancy concentrations in the surface shell, and the lateral gradients in the core lattice are small and can be neglected.

In this case, the total number of vacancies in the nanoparticle can be given as

$$n = n_v + n_s$$

(26)

and the nanoparticle consists of \( N \) atoms, with \( N_i \) atoms lying on the surface and \( N_c \) atoms located in the core:

$$N = N_i + N_c$$

(27)

Then the vacancy concentration in the core and the surface shell can be respectively given by

$$X_v^{sp} = \frac{n_v}{n_v + N_c}$$

(28a)

$$X_v^{sp} = \frac{n_s}{n_s + N_i}$$

(28b)

Thus, the total number of vacancies is

$$n = X_v^{sp} \frac{N}{1 - X_v^{sp}} N_i + X_v^{sp} \frac{N_i}{1 - X_v^{sp}}$$

(29)

The concentration of vacancies in the nanoparticle is

$$X_v^{sp} = \frac{N X_v^{sp} N_i + X_v^{sp} N_i}{N - X_v^{sp} + N_i - X_v^{sp} N_i}$$

(30)

Because of \( X_c \ll 1 \) and \( X_s \ll 1 \), \( eq \ 30 \) can be reduced to

$$X_v^{sp} = \frac{NX_v^{sp} + NX_v^{sp}}{N + N_i}$$

(31)

The number of atoms in the core and the surface shell is calculated from \( N_c = V_{c,v}/V_c \) and \( N_i = V_{s,v}/V_s \) respectively, where \( V_c \) and \( V_s \) denote the vacancy-free atomic volume in the core and the surface shell.

The vacancy concentrations in the core and the surface shell are calculated from the equivalent chemical potentials and are given by

$$X_v^{sp} = X_v^{sp} \exp \left( \frac{\sigma V_{c,v} \Omega_b}{k_B T R_{c0}} \right) = X_v^{sp} \exp \left( - \frac{2 \sigma V_{c,v} \Omega_b}{k_B T R_{c0}} \right)$$

(32a)

$$X_v^{sp} = X_v^{sp} \exp \left( \frac{\Delta \mu^0 + 2 \sigma (V_{c,v} \Omega_b/R_{c0} + V_{s,v}/3)}{k_B T} \right)$$

(32b)

where the generalized capillary equation is used. The surface stress is calculated from
\[
\sigma_i = \frac{3\sigma_0}{\Psi} + \frac{Y_{s,Y}}{\Psi} \left( \frac{V_{s,Y}^c V_{s,Y}^p}{V_{s,Y}} \right) \left( \Psi - \frac{V_{s,Y}^p}{V_{s,Y}} \right)
\]

(33)

Solving eqs 32 and 33 determines the surface stress and the concentration simultaneously, when the surface eigenstress and the material properties are available.

3. RESULTS AND DISCUSSION

The intrinsic surface elastic parameters and bulk vacancy formation energy of different materials are summarized in Table 1. The following figures illustrate analytical results at room temperature \( T = 300 \) K. Atomic volume for all metals in the core and the surface shell used in calculating these plots is approximately \( V_c \approx 1 \times 10^{-29} \) m\(^3\) and \( V_s = 1.1 \times 10^{-29} \) m\(^3\), respectively. Although vacancy concentration can vary with the surface shell thickness, the vacancy concentration variation trend with the particle size remains almost the same. It is widely accepted that the interfacial thickness can vary from 0.5 to 2 nm. In the present work, we assume that the surface shell thickness is 1 nm. For simplicity, the modulus and Poisson’s ratio of the core and the shell are assumed to be independent of the vacancy concentration. The Poisson’s ratio of the surface shell is assumed to be 0.3. The vacancy formation volume in the core and the surface shell is assumed to be 0.7 \( \times 10^{-29} \) m\(^3\) and 0.66 \( \times 10^{-29} \) m\(^3\), respectively. We assumed that the difference between the reference chemical potential in the surface shell and the core is \( \Delta \mu_0 = 100 \) meV.

Parts a and b of Figure 1 show that the vacancy concentration in the core and the surface shell present the same trend for all metallic particles, which decreases when the particle size is reduced, and this difference is significantly larger when the particle size is reduced to few tens of nanometers. The vacancy concentration approaches an infinitesimal value when the particle size is lower than 10 nm. Figure 1c shows that the vacancy concentration in the surface shell is much higher than that in the core, and this phenomenon becomes more significant when the particle size gets smaller, which is in agreement with experimental measurements. Although the vacancy concentration in the core and the surface both decrease with the particle size, the apparent concentration in the whole particle exhibits a different behavior. When the particle size is reduced, the apparent concentration first increases and reaches a maximum value at dozens of nanometers particle size, and then rapidly decreases to a very small value. As mentioned above, the influence of surface stress for metal nanoparticles considered in this paper will result in a decrease of both core and surface vacancy concentration. However, the fraction of the surface shell in total particle gets larger when particle size is reduced, which leads to variation of apparent vacancy concentration. Thus, the appearance of the peak value of the apparent vacancy concentration is due to competition of the surface stress and the surface fraction in total particle. Obviously, the Pt particles show the largest difference in vacancy concentration compared to other particles.

Parts a and b of Figure 2 show that the lattice and the sample strains vary with the particle size for different metallic particles. The strains increase significantly when the particle size decreases below 100 nm. From eqs 14 and 16, both strains are caused by the surface stress and the vacancy concentration. Vacancy concentration is very small at 300 K, so the strain caused by vacancy concentration can be ignored. The strains in

![Figure 1](https://example.com/fig1.png)

Figure 1. Vacancy concentration (a) in the core and (b) the surface shell to the bulk ratio, (c) the vacancy concentration in surface shell to core ratio, and (d) the apparent vacancy concentration in particles to the bulk ratio, all as functions of the particle size for Ni, Cu, Au, and Pt.
parts a and b of Figure 2 are caused primarily by the surface stress. From eqs 15 and 33, the surface stress and lattice stress in parts c and d of Figure 2 can be caused by the surface stress and vacancy concentration, presenting the same trend with the strain. As expected for all metallic particles, the surface stress decreases when particle size decreases to a few nanometers. The lattice stress shows an opposite sign with the surface eigenstress and increases exponentially with the reduced particle size. When the particle size is extremely large, the lattice stress decreases to zero. Clearly, Pt particles show the largest surface stress compared to other particles, causing the largest variation in the vacancy concentration change.

4. CONCLUSIONS

Present work is based on the thermodynamic analysis, which requires that the nanoparticles obey basic thermodynamic laws and principles. The intrinsic elastic parameters introduced in present work are determined from atomistic simulations in our previous work. The apparent vacancy concentration in spherical nanoparticle is calculated by taking into account both the core and the surface defects concentration. Notwithstanding both the vacancy concentration in the core and the surface shell for Ni, Cu, Au, and Pt particles, it can be greatly decreased as the particle size is decreased. The apparent vacancy concentration in the whole nanoparticle reaches the maximum at the critical particle size of about 100 nm and is lower for larger or smaller particles. This phenomenon can be explained by the competition effects of the surface stress and the surface fraction in the total particle.

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Notes
The authors declare no competing financial interest.

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