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Thermodynamic study on the melting of nanometer-sized gold particles on graphite substrate

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Surface tension plays an important role in lowering the melting temperature of nanometer-sized particles, but whether the surface tension determined in macro scale is valid for the nanometer-sized particles is unclear. Moreover, the melting of the nanometer-sized particles formed on solid substrates can be affected by interfacial tension, but no research has been reported on the effect of substrates on the melting temperature. Therefore, in order to predict the melting temperature of nanometer-sized metallic particles on solid substrates, thermodynamic parameters such as surface tension and interfacial tension should be properly estimated. In the present work, thermodynamic assesment is given on the melting temperature of gold particles in nanometer-size placed on a graphite substrate. Surface tension of liquid gold and the contact angle between liquid gold and the graphite substrate are measured by the constrained drop method and the sessile drop method in macro scale, respectively. Then, the effect of the graphite substrate on the melting temperature of nanometer-sized gold particles are examined by thermodynamic calculations minimizing the total Gibbs free energy, the sum of bulk, surface and interface energies. It is found that the graphite substrate has negligible effect on the melting temperature of nanometer-sized gold particles. Thermodynamic assessments provide that the surface tension of solid gold is 1.339 N/m at 1373 K and that the decrease in the surface tension of liquid gold with size will be considerable for the particles smaller than ~5 nm.

1. Introduction

Surface tension plays an important role in thermodynamic assesement of the melting temperature of nanometer-sized metallic particles. Clearly, it is expected that as the size of a particle decreases, the ratio of surface to volume considerably increases and the melting temperature decreases. The decrease in the melting temperature has been reported by many researchers for pure metallic systems (gold [1], tin [2], lead [3], indium [3], bithmuth [4], etc.) and alloy systems [5–7].

Since the melting of nanometer-sized particles had been investigated on solid substrates, interface tension, as well as surface tension, might also affect the melting temperature of nanometer-sized partilces. However, previous researches did not consider the effect of substrates on the melting temperature.

When we treat small particles with thermodynamics, the applicability of the bulk data is doubtable, especially surface tension. Many researchers pointed out the possibility of the surface tension change in small particles [8–15]. Thermodynamically, the position of the hypothetical Gibbs surface is chosen as the zero adsorption surface, which slightly differ from the surface of tension due to the curvature of the particle [8, 9]. Therefore, we may expect that the surface tension of nanometer-sized particles have different value from that of macro scale.

In the present study, the melting temperatures of nanometer-sized gold particles on graphite substrates were examined by minimizing the total Gibbs free energy of bulk, surface and interfacial energies. Then the effect of the graphite substrate on the melting temperature of nanometer-sized gold particles has been estimated. For the thermodynamic assessments, surface tension of liquid gold and the contact angle between liquid gold and a graphite substrate were determined by the constrained drop method and the sessile drop method, respectively. The possibility of the surface

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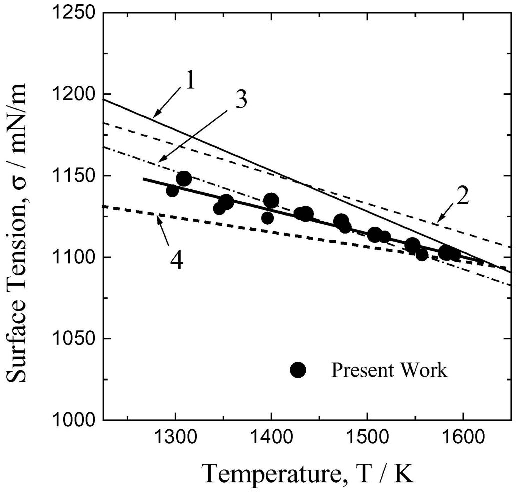

Figure 1 Surface tension of liquid Au as a function of temperature. (1: Iida and Guthrie [20], 2: Suggested by Keene [19], 3: Mean of reported values [19], 4: Egry *et al*. [21].

tension changes was alos examined by using Tolman's model [8, 9].

2. Experimental results

2.1. Surface tension of liquid Au

Highly reliable surface tension of liquid Au was obtained by the constrained drop method. In this experiment, an alumina crucible was used to make a large axi-symmetric drop. In addition, a high-resolution CCD camera for investigation, an additional CCD camera for level-investigation, and a He-Ne laser were used to get clear surface profile information. Experimental details and improved precision of measurements can be found in our other literatures [16–18]. In Fig. 1, the surface tension of liquid Au is shown. For comparison, the reported $\sigma - T$ relations after Keene [19], Iida and Guthrie [20] and Egry *et al.* [21] are also plotted. Keene [19] reviewed previous measurements and found that the measurements by the levitation method have higher value than the sessile drop method. He thought that the lower values with the sessile drop method had been caused by the contamination from the substrate, and suggested that the mean of highest values would be close to the true surface tension. However, Egry *et al.* [21] showed that electromagnetic force in the levitation method would increase the apparent surface tension values by 5–15%, and measured more accurate surface tension values considering the effect of electromagnetic force. His measurements show reasonable accordance with the reported mean values [19] which had been considered lowly estimated. The present results also show good accordance with those by Egry *et al.* [21] In addition, the present results show much smaller relative errors from the mean value (±0.5%) than those by Egry *et al.* [21](±2.7%).

2.2. Contact angle between liquid Au and solid graphite

Generally, in the liquid-metal/solid-substrate systems, the interface tension can easily be obtained by the Young's relation:

$$\sigma_{\mathrm{SL}} = \sigma_{\mathrm{SV}} - \sigma_{\mathrm{LV}} \cos\theta \qquad (1)$$

where σ_{SL} and σ_{SV} are interface tensions between solid and liquid and between solid and vapor phases. σ_{LV} is the surface tension of liquid and θ is the contact angle. In order to estimate the interface tension between gold and graphite, the information of the contact angle and the surface tension of solid substrate is necessary.

The contact angle between liquid gold and solid graphite was measured by the sessile drop method at 1336 K. Even though liquid gold has solubility of carbon (∼0.3 mass% at 1336 K) [22], the contact angle does not change so much after contacting with each other and shows very large constant value, 146 deg. According to this, the contact angle between gold and graphite is assumed constant in the following thermodynamic calculations. The surface tension of solid graphite is taken from ref. 23.

3. Thermodynamic calculation

Fig. 2 shows a schematic illustration of a nanometer-sized gold particle on a solid substrate: (1) absolutely non-wetting system (θ (contact angle) = 180 deg.), (2)

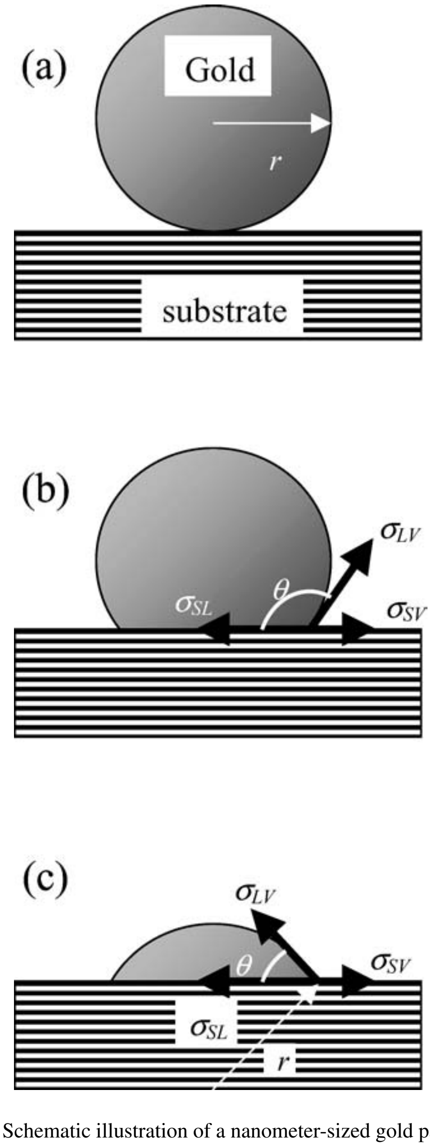

Figure 2 Schematic illustration of a nanometer-sized gold particle on a solid substrate: (a) absolutely non-wetting system (θ (contact angle) = 180 deg.), (b) non-wetting system (90 deg. < 180 deg.) and (c) wetting system (θ < 90 deg).

non-wetting system (90 deg. $<$ 180 deg.) and (3) wetting system ($\theta < 90$ deg). For non-wetting system., the partticle size (usually given as the maximum radius, $r_{\mathrm{Max.}}$) is the same as the curvature radius (r), whereas it is smaller than the curvature radius for wetting system. In any case, the total Gibbs free enrgy of a solid particle ($G^{\mathrm{S}}_{\mathrm{Au}}$) is the sum of bulk, surface and interface energies.

$$G^{\mathrm{S}}_{\mathrm{Au}} = G^{\mathrm{S,o}}_{\mathrm{Au}} \times n_{\mathrm{Au}} + \sum \left(\sigma^{\mathrm{S}}_{\mathrm{Au,j}} \times \mathrm{S}^{\mathrm{S}}_{\mathrm{j}}\right) + \sigma^{\mathrm{S}}_{\mathrm{Au/C}} \times I^{\mathrm{S}} \quad (\mathrm{J}) \tag{2}$$

If solid gold particles are assumed as spherical ones, the effects of crystal faces (*j*) on the surface tension of solid can be ignored, and then Equation 2 can simply expressed as Equation 3

$$G^{\mathrm{S}}_{\mathrm{Au}} = G^{\mathrm{S,o}}_{\mathrm{Au}} \times n_{\mathrm{Au}} + \sigma^{\mathrm{S}}_{\mathrm{Au}} \times S^{\mathrm{S}} + \sigma^{\mathrm{S}}_{\mathrm{Au/C}} \times I^{\mathrm{S}} \quad (\mathrm{J}) \tag{3}$$

When the solid gold is converted into liquid, the totoal Gibbs free energy can be written by Equation 4.

$$G^{\mathrm{L}}_{\mathrm{Au}} = G^{\mathrm{L,o}}_{\mathrm{Au}} \times n_{\mathrm{Au}} + \sigma^{\mathrm{L}}_{\mathrm{Au}} \times \mathrm{S}^{\mathrm{L}} + \sigma^{\mathrm{L}}_{\mathrm{Au/C}} \times I^{\mathrm{L}} \quad (\mathrm{J}) \tag{4}$$

where $G^{\alpha,\mathrm{o}}_{\mathrm{Au}}$ is the standard molar Gibbs free energy of gold (J/mol) in the phase of $\alpha (= S$(solid) or L(liquid)), n_{Au} is the number of gold atoms (mol) in a nano-sized particle, $\sigma^{\alpha}_{\mathrm{Au}}$ is the surface tension of gold (N/m), S^{α} is the surface area of the particle (m^2), $\sigma^{\alpha}_{\mathrm{Au/C}}$ is the interfacial tension and I^{α} is the interface area between the particle and the graphite substrate.

If we assume that the physical and thermodynamic properties do not change with paritcle size, the total number of gold atoms is calculated using the molar volume of solid gold ($\overline{V^{\mathrm{S}}_{\mathrm{Au}}}$).

$$n_{\mathrm{Au}} = \frac{V^{\mathrm{S}}_{\mathrm{Au}}}{\overline{V^{\mathrm{S}}_{\mathrm{Au}}}} \quad (\mathrm{mol}) \tag{5}$$

When the contact angle between gold and graphite is given, the volume of a gold particle is obtained from Equation 6.

$$V^{\mathrm{S}}_{\mathrm{Au}} = \frac{\pi}{4} r^{\mathrm{S}^3}_{\mathrm{Au}} \left[3(1 - \cos\theta) - \frac{1}{3}(1 - \cos 3\theta)\right] \quad (\mathrm{m}^3) \tag{6}$$

Becasue the volume of gold increases by the phase transformation from solid to liquid, the volume of a liquid gold drop is evaluated from Equation 7.

$$V^{\mathrm{L}}_{\mathrm{Au}} = n_{\mathrm{Au}} \times \overline{V^{\mathrm{L}}_{\mathrm{Au}}} \tag{7}$$

Here, the molar volume of liquid gold $\overline{V^{\mathrm{L}}_{\mathrm{Au}}}$ is given as a function of temperature. Then, the radius of a liquid drop is expressed as Equation 8.

TABLE I The values of the thermodynamic qunataties used in the calculations of melting temperature of gold particles on graphite substrates

Variables	Equations	Ref
Surface tension (Nm^{-1})	$\sigma^{\mathrm{L}} = 1.330 - 0.00014 \cdot T$	Present work
	$\sigma^{\mathrm{S}} = 1.948 - 0.00043 \cdot T$	24
	$\sigma_{\mathrm{Graphite}} = 1.174 - 0.00013 \cdot T$	23
Molar volume (m^{3}mol^{-1})	$V^{\mathrm{L}} = 11.3 \times 10^{-6}$ $(1.0 + 0.000069 \cdot (T - 1336.15))$	20
	$V^{\mathrm{S}} = 1.07109 \times 10^{-5}$	20
Gibbs free energy change of melting / (Jmol^{-1})	$\Delta G^{\mathrm{LS}} = G^{\mathrm{L}} - G^{\mathrm{S}} = 12552.0 - 9.385866 \cdot T$	25
Contact angle (deg.)	$\theta = 146$	Present work

$$r^{\mathrm{L}}_{\mathrm{Au}} = \left(\frac{4V^{\mathrm{L}}_{\mathrm{Au}}}{3(1 - \cos\theta) - \frac{1}{3}(1 - \cos 3\theta)}\right)^{1/3} \tag{8}$$

The surface area of a gold particle and the interface area between the particle and the substrate are then given as follows.

$$S^{\alpha} = 2\pi R^{\alpha^2}_{\mathrm{Au}}(1 - \cos\theta) \tag{9}$$

$$I^{\alpha} = \pi r^{\alpha^2}_{\mathrm{Au}} \sin^2\theta \tag{10}$$

It is calculated that the change in the radius by melting at 1336 K is only +1.80%, and those of the surface and interface area are both +3.63%.

In this calculation, the interfacial tension between gold and graphite was estimated using Young's relation (11), by assuming that the contact angle is not affected by the particle size or phase transformation from solid to liquid.

$$\sigma^{\alpha}_{\mathrm{Au/C}} = \sigma_{\mathrm{Graphite}} - \sigma^{\alpha}_{\mathrm{Au}} \cos\theta \tag{11}$$

Using Equation 3–11, the melting temperature is determined as $G^{\mathrm{S}}_{\mathrm{Au}}$ and $G^{\mathrm{L}}_{\mathrm{Au}}$ have the same value. In Table I, the data used in the present calculations are summarized.

4. Discussion

4.1. Effects of substrate and isotropic solid surface

In Fig. 3, the calculated results are shown with experimental results by Sambles *et al.* [1] Dashed lines (1) and (2) are, respectively, the results with the data in Table 1 for the absolutely non-wetting system and the non-wetting system (θ 146 deg.). The contact angle (θ is simply assumed constant regardless of the particle size. From Fig. 3, it is found that there is no difference in the calculated melting temperatures. However, the results of lines (1) and (2) show slightly smaller values than experimental results. Probably, one may consider that the contact angle for nanometer-sized particle is different from the value obtained in macro scale, i.e.,

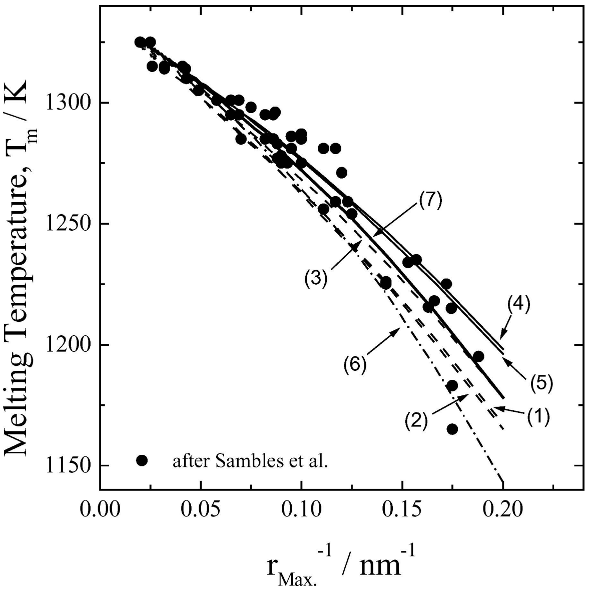

Figure 3 Melting temperature of nanometer-sized gold particles placed on graphite substrates as a function of the maximum radius.

the interface tension decreases with decreasing the particle size for some reasons such as line tension [26–28]. With decreasing the contact angle, the melting temperature can slightly increase and reaches a peak when the contact angle is 90 deg, after then it dropped dramatically. Thus, the maximum values are obtained by assuming that the contact angle is 90 deg. (dashed line (3)). In this case, the particle size (maximum radius) is smaller than the curvature radius, so that the curvature radius is obtained from Equation 12.

$$r = r_{\mathrm{Max.}}/\sin\theta \qquad (12)$$

However, the calculation results with the contact angle of 90 deg are almost the same as lines (1) and (2). Because the contact angle in metal/graphite systems larger than ∼5 nm is generally higher than 90 deg [29, 30], we may conclude that graphite has no effect on the melting temperature of nanometer-sized gold particles on graphite substrates.

Another possible reason for the discrepancy between calculations and measurements is that the surface tension of solid god has been assumed as the value obtained from experiments of the zero creep test. In the experiments, the surface tension of solid gold is obtained as a mean value of anisotropic multi-crystal, while nanometer-sized metallic particles have facet surfaces. Hence, the mean surface tension value does not yield the surface tension of a particular surface facet. Wan *et al.* [31] calculated the surface tension of solid gold with the modified embedded atom method, and obtained the surface tension of (111), (100) and (110) surfaces of gold at 0 K as 866, 1032 and 987 mN/m, respectively. It seems that the absolute values have been lowerly estimated, nevertheless we may refer the ratio of the maximum to the minimum surface tension, 1.19. Thus, we may expect that the surface tension of solid gold in the calculation of melting temperature may have larger or smaller value than those obtained from experiments by ±10%. In Fig. 3, the surface tension of solid gold has been modified to predict the overall trend in the data. The best fits of solid lines (4) and (5) for the non-wetting system (θ 146 deg.) and the absolutely non-wetting system (θ 180 deg.) are given with the surface tension of solid gold decreased by 2.5%, respectively, i.e., the surface tension of solid gold at 1373 K is 1.339 N/m. Here, it is noticable that the measurements of the particles smaller than ∼7 nm are slightly lower than the calculation results. In the follwing section, we will discuss on this matter.

4.2. Effect of decrease in surface tension

If we simply assume that the surface tension may change due to the curvature of small particles, the surface tension of solid gold particles and the interface tension would not be changed, because solid has a flat surface. However, there is possibility that the surface tension of liquid decreases. Tolman firstly suggested that the surface tension would decrease when the size of a particle is small enough, and derived his well-known Equation (13) [9].

$$\frac{\sigma}{\sigma^{\infty}} = \frac{1}{(1 + 2\delta/r)} \qquad (13)$$

where σ^{∞} is the surface tension of a plane surface, and δ is the Tolman parameter, the difference between the zero adsorption surface and the surface of tension. If we assume that $\delta(>0)$ is a constant value, the surface tension would decrease with decreasing the radius of the particles.

Samsonov *et al.* [15] in his calculations showed that the Tolman parameter in metallic system is the same as the effective ionic radius. Then, the Tolman parameter for liquid gold can be assumed as 0.137 nm [32]. The line (6) in Fig. 3 represents the calculation results considering the surface tension decrease of liquid gold with the particle size by Equation 13. It is found that the calculation results show somehow lower values than the measurements. If we draw a line by adjusting the Tolman parameter, it is found that the Tolman parmeter cannot exceed 0.05 nm. (line (7) in Fig. 3) Then, the surface tension for the particle of $r = \sim 5$ nm shows only 1% surface tension drop. However, we may anticipate that the melting temperature of gold particles smaller than ∼5 nm can largely be affected by the surface tension decrease.

5. Conclusion

The effect of the graphite substrate on the melting temperature of nanometer-sized gold particles has been examined by thermodynamic calculations. It is found that the graphite substrate has negligible effect on the melting temperature of nanometer-sized gold particles. Thermodynamic assessments provide that the surface tension of solid gold is 1.339 N/m at 1373 K and that the decrease in the surface tension of liquid gold with size will be considerable for the particles smaller than ∼5 nm.

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