Material Properties and characterization
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On the Melting of Nanoparticles
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1.1 Introduction

Driven by the continuous need for advancement in the state of the art of micro- and nanomanufacturing in a host of fields, exemplified prominently by electronics, new methodologies and processes need to be developed, after overcoming formidable scientific challenges, to engineer nanostructures with desired properties and functionality. At the same time, the emergence of consistent manufacturing methods of ultra fine particles (UFP) (or, after the more popular terminology-nanoparticles) of many materials, is creating a vivid activity related to their utilization. The potential they possess through remarkable thermophysical properties (significantly different than those of their bulk counterparts), can play a pivotal role in the development of emerging technologies of the kind mentioned above. The reason for using nanoparticles in this work lies in the significant melting temperature depression compared to their bulk counterpart (Buffat and Borel, 1976).

The handling of nanoparticles by themselves is difficult because a dust free and inert atmosphere is needed. Schaefer \textit{et al.} (1995) and Ben Ali \textit{et al.} (2002) manipulated single nanoparticles with an atomic force microscope whereas Krinke \textit{et al.} (2001) directly deposited nanoparticles on a Si substrate from the gas phase attracted by charge patterns (created by contact charging) and Xu \textit{et al.} (2004) used laser-based direct deposition of nanoparticles from the gas phase on a substrate to build one- and two-dimensional structures. Another method to handle nanoparticle is their dispersion in a carrier-liquid, a so called nanoparticle suspension or nanoink. Many applications utilize nanoparticle suspensions with a volatile solvent as carrier-liquid which evaporates naturally or by heating leaving the nanoparticles in the desired two- or three-dimensional structures, either by self assembling (Maillard \textit{et al.}, 2000; Stowell and Korgel, 2001; Shah et al., 2003) or in combination with
pre-patterning the substrate (Liu et al., 2002; Santhanam et al., 2003), or by using prefabricated traces or moldings to fill with the nanoparticle suspension (Rogers et al., 1998; Iwashige et al., 2001) or by printing the nanoink into the desired pattern (He et al., 2000; Fuller et al., 2002; Szczech et al., 2002; Huang et al., 2003; Magdassi and Ben Moshe, 2003; Voit et al., 2003). The self assembling technique is restricted by the limited number of possible patterns without pre-patterning and the pre-patterning itself counteracts the simplicity of the process. Printing nanoink with drop-on-demand (DOD) ink jet technology was accomplished by several authors who attempted different methods to produce conductive patterns and to manipulate the feature size. Szczech et al. (2002) baked the printed nanoink pattern in the oven. The achievable feature size of O (120 µm) is limited by the smallest droplet-size of the DOD ink jet printer. In order to reduce the features size of the printed line, Fuller et al. (2002) heated the substrate to evaporate the carrier-liquid upon impact and subsequently baked the nanoparticles in the oven. He et al. (2000) fabricated designed architectures of Au nanoparticles with printed self-assembled monolayer as templates. Organic-encapsulated gold nanoparticles are printed and subsequently annealed at temperatures < 200 °C to form low resistance conductor pattern by Huang et al. (2003).

The reason for using nanoparticles lies in the scientifically reduced melting temperature of approximately 400 °C for single nanoparticles with a mean diameter of 4 nm compared to 1063 °C for bulk gold (Buffat and Borel, 1976). Microfabrication of electronics and mechanical structures are commonly accomplished with lithography which is a time consuming expensive process. The use of DOD ink jet printer is an alternate approach of depositing conducting material on a substrate with the advantage of the precise drop wise deposition of small amounts of liquid at desired locations saving expensive materials. In lithography a metal coating is applied over the entire substrate, followed by a photoresist. A mask of the line pattern is placed on the photoresist. After exposure, the developed photoresist prevents the covered metal from being etched away in a chemical bath. This chemical etching produces highly toxic waste which is not an issue of the introduced method. Drop-on-demand ink jet printing is successfully used for MEMS packaging with molten solder picoliter droplets (Hayes et al., 1992; Attinger et al., 2000; Haferl et al., 2000; Haferl and Poulakakos, 2003), metallo-organic decomposition ink (Teng and Vest, 1988) and organic light emitting materials (Bharathan and Yanga, 1998; Hebner et al., 1998; Percin G, 1998; Sirringhaus et al., 2000; Calvert et al., 2002; Blanchet et al., 2003; Burns et al., 2003) but the usage of molten
gold requires temperatures higher than the melting point of bulk gold (1063 °C) which exceeds the temperature range of ink jet technology.

### 1.2 Melting point reduction of nanoparticles

The influence of the surface and in particularly its shape (curvature) on the melting point of a material is gaining importance with decreasing size of the sample (particle) under investigation. The effect of surface energy on the melting of small particle was first considered in 1909 by Pawlow (1909a; 1909b) who predicted that there would be a change in melting point from the bulk value inversely proportional to the particle radius. He identified the melting temperature as the temperature (triple point) where a solid particle and a liquid particle of identical mass and their vapor are in equilibrium. Technical difficulties prevented an experimental proof until Takagi (Takagi, 1954) observed this effect on thin metal films in 1954. Several authors conducted experiments on different materials and particle sizes and defined different theoretical models to explain the so called “thermodynamic size effect” (Reiss and Wilson, 1948; Hanszen, 1960; Semenchenko, 1962; Wronski C. R. M., 1967; Sambles, 1970; Sambles et al., 1970; Berman and Curzon, 1974; Peppiatt, 1975; Peppiatt and Sambles, 1975; Buffat and Borel, 1976; Curzon et al., 1976; Hasegawa et al., 1980). Sambles (1970) compared in his thesis his experimental results with three different theories assuming a) equilibrium of a solid particle, a liquid particle and their vapor (Pawlow, 1909a; Pawlow, 1909b), b) equilibrium of a solid particle within an infinite liquid (Rie, 1923) and c) equilibrium of a solid body surrounded by a thin liquid layer which in turn is surrounded by vapor (Reiss and Wilson, 1948; Hanszen, 1960; Wronski C. R. M., 1967). He derived the equations for the melting temperature reduction again and fit the unknown parameters in the equations with values evaluated in his experimental data. He rejected the theory b) of the solid particle within a liquid and found for the other two theories correspond well with his experimental results.

The reduced melting temperature, $T$, for a simultaneous existence of a solid particle and liquid particles of identical mass and a vapor phase reads (Pawlow, 1909a; 1909b; Sambles, 1970):
where $T_m$ is the melting temperature of the bulk phase, $\Delta h_{ls}$ is the latent heat of melting, subscripts $s$, $l$ and $v$ mean solid, liquid and vapor, $\rho$ and $\gamma$ is the density and the surface tension, respectively. The theory of Pawlow predicts too high temperatures for small particles (Borel, 1981).

The temperature reduction of a solid particle embedded in a thin molten layer surrounded by a vapor phase is given by (Hanszen, 1960; Sambles, 1970):

$$1 - \left( \frac{T}{T_m} \right) = \frac{2}{\rho, \Delta h_{ls} r_s} \left[ \gamma_{ns} - \gamma_{nl} \left( \frac{\rho_s}{\rho_l} \right)^{\gamma_l} \right]$$  \hspace{1cm} (1.1)

where $r_s$ is the radius which would characterize the particle at its melting point assuming that it remains entirely in the solid form, $\delta$ is the liquid layer thickness and $\gamma_{sl}$ is the solid-liquid interfacial tension.

Buffat and Borel (1976) measured the melting temperature of gold particles having diameters down to 20 Å and compared the results with the two investigated and accepted phenomenological models by Sambles (1970). They derived the reduced melting temperature for a simultaneous existence of a solid particle and liquid particles of identical mass and a vapor phase of Pawlow again and extended the derivation by considering a higher-order approximation of the chemical potential leading to:

$$\ln \left( \frac{T}{T_m} \right) = \frac{2}{\rho, \Delta h_{ls} r_s} \left[ \gamma_{ns} - \gamma_{nl} \left( \frac{\rho_s}{\rho_l} \right)^{\gamma_l} \right] \left[ \gamma_{ns} \left( \frac{\rho_s}{\rho_l} \right)^{\gamma_l} \right]^{-1}$$  \hspace{1cm} (1.2)

where $r_s^*$ is the radius which would characterize the particle at its melting point assuming that it remains entirely in the solid form, $\delta$ is the liquid layer thickness and $\gamma_{sl}$ is the solid-liquid interfacial tension.

Buffat and Borel (1976) measured the melting temperature of gold particles having diameters down to 20 Å and compared the results with the two investigated and accepted phenomenological models by Sambles (1970). They derived the reduced melting temperature for a simultaneous existence of a solid particle and liquid particles of identical mass and a vapor phase of Pawlow again and extended the derivation by considering a higher-order approximation of the chemical potential leading to:

$$0 = \Delta h_{ls} \left[ 1 - \frac{T}{T_m} \right] - \frac{2}{\rho, r_s} \left[ \gamma_{ns} - \gamma_{nl} \left( \frac{\rho_s}{\rho_l} \right)^{\gamma_l} \right] + \frac{c_{ps} - c_{pl}}{2} T_m \left( 1 - \frac{T}{T_m} \right)^2 -$$

$$- \frac{2}{\rho, r_s} \left[ \gamma_{ns} \left( \eta_s - 2 \alpha_s \right) - \gamma_{nl} \left( \eta_l - 2 \alpha_l \right) \left( \frac{\rho_s}{\rho_l} \right)^{\gamma_l} \right] T_m \left( 1 - \frac{T}{T_m} \right) + \frac{2}{\rho, r_s^*} \left[ \chi_s \gamma_s^2 - \chi_l \gamma_l^2 \left( \frac{\rho_s}{\rho_l} \right)^{\gamma_l} \right]$$  \hspace{1cm} (1.3)

where $c_p$ is the specific heat capacity at constant pressure, $\eta = -(1/\gamma) \partial \gamma / \partial T$, $\alpha$ and $\chi$ is the linear-expansion coefficient and isothermal compressibility coefficient, respectively. Neglecting the second order terms of Eq. (1.3) leads to the same equation as derived by Pawlow (Eq. (1.1)).
The “thermodynamic size effect” is still investigated with new more accurate experimental methods and improved phenomenological models (Borel, 1981; Solliard, 1984; Frenken et al., 1986; Garrigos et al., 1989; Nenow and Trayanov, 1990; Wautelet, 1991; Kofman et al., 1994; Lai et al., 1996; Bachels and Güntherodt, 2000) and with molecular dynamics simulations (Ercolessi et al., 1991; Chushak and Bartell, 2001; Arcidiacono et al., 2004).

![Graph](image)

Fig. 1.1: Melting temperature of gold particles as a function of particle radius for two models: a) a simultaneous existence of a solid particle and liquid particles of identical mass and a vapor phase (Pawlow, 1909b; Sambles, 1970) and b) solid particle embedded in a thin molten layer surrounded by a vapor phase (Hanszen, 1960; Sambles, 1970). All needed physical values are taken from Buffat and Borel (1976).
The reduced melting temperature of small particles can be derived in the following way. Consider a one component capillary system consisting of two phases, a continuous $\alpha$ phase and a $\beta$ phase, which is a spherical drop of radius $r$ within the phase $\alpha$, in equilibrium. Phase $\beta$ is a pure liquid drop and the $\alpha$ phase is its vapor. Figure 1.1 shows a capillary system consisting of two phases with liquid / vapor interface. The freely moving piston maintains a constant pressure of phase $\alpha, p_\alpha$.

![Diagram showing a capillary system with liquid and vapor phases](image)

*Fig. 1.2: Concept of a capillary system of two phases with liquid / vapor interface. The freely moving piston maintains a constant pressure $p_\alpha$ inside the system.*

Assuming that a differentially small amount of the droplet evaporates under constant vapor pressure, the Gibbs-Duhem equation for the two phases is:

Phase $\alpha$: 

$$s_\alpha dT + \frac{N_\alpha}{m_\alpha} d\mu_\alpha = 0$$ (1.4)

Phase $\beta$: 

$$s_\beta dT - v_\beta dp_\alpha + \frac{N_i}{m_i} d\mu_i = 0$$ (1.5)

Where $N_i$ is the number of atoms in the i phase. The chemical potential, $\mu_i$, includes the surface energy of the phase.

The free energy change over the entire system, $G_T$, at equilibrium is zero, because $G_T$ is a minimum at equilibrium

$$\mu_v = \mu_i$$ (1.6)
\[ d\mu_v = d\mu_i \] (1.7)

The subtraction of Eq. (1.5) from Eq. (1.4) together with Eq. (1.6) yields:

\[ (s_v - s_i) dT + \nu_i d\rho_i = 0 \] (1.8)

The Laplace equation (with \( dp_v = 0 \)) is defined as:

\[ dp_i = d\left(\frac{2\gamma_{iv}}{r}\right) \] (1.9)

Substituting Eq. (1.9) into Eq. (1.8) and using the latent heat of evaporation, \( \Delta h_{vl} \) which is defined as \( \Delta h_{vl} = T(s_v - s_i) \), results in:

\[ \left(\frac{\Delta h_{vl}}{T}\right) dT + \nu_i d\left(\frac{2\gamma_{iv}}{r}\right) = 0 \] (1.10)

The accurate solution of Eq. (1.10) by integration from \( \infty \) to \( r_l \) with the assumption \( \Delta h_{vl} \neq f(r) \) yields:

\[ \int_{r_0}^{r_l} \frac{dT}{T} = -\frac{\nu_i}{\Delta h_{vl}} \left[ d\left(\frac{2\gamma_{iv}}{r}\right) \right] \] (1.11)

\[ \ln \left(\frac{T}{T_0}\right) = -\frac{\nu_i}{\Delta h_{vl}} \left(\frac{2\gamma_{iv}}{r_i}\right) \] (1.12)

Equation (1.12) is well known as the Thompson equation where \( T_0 \) is the temperature of the bulk material.

Solving Eq. (1.12) by a Taylor series of the logarithm accurate to 1\(^{\text{st}}\) order the equation results in:

\[ \frac{\Delta T}{T_0} = \frac{T - T_0}{T_0} = -\frac{\nu_i}{\Delta h_{vl}} \left(\frac{2\gamma_{iv}}{r_i}\right) \] (1.13)
The influence of curvature on the equilibrium temperature of a solid particle with its vapor can be similarly derived. The phase $\beta'$ is a pure solid particle and the phase $\alpha'$ is its vapor. The pressure $p_\alpha'$ is again constant. The Gibbs-Duhem equations for the two phases are:

Phase $\alpha'$:

$$s_\alpha dT + \frac{N_\alpha}{m_\alpha} d\mu_\alpha = 0 \quad (1.14)$$

Phase $\beta'$:

$$s_\beta dT - \nu_\beta dp_\beta + \frac{N_\beta}{m_\beta} d\mu_\beta = 0 \quad (1.15)$$

Again the change in the Gibbs energy of the whole system is zero and therefore the change in the chemical potential is zero, resulting again in $d\mu_\alpha = d\mu_\beta$. Neglecting the crystalline structure of the solid by assuming a perfect spherical particle the Laplace equation is (with $dp_\nu = 0$):

$$dp_\nu = d \left( \frac{2\gamma_{sv}}{r} \right) \quad (1.16)$$

Similar to the previous case Eq. (1.14) is subtracted from Eq. (1.15) and the latent heat of sublimation, $\Delta h_{sv}$, which is defined as, $\Delta h_{sv} = T(s_\alpha - s_\gamma)$ together with Eq. (1.16) results in:

$$\left( \frac{\Delta h_{sv}}{T} \right) dT + \nu_\gamma d \left( \frac{2\gamma_{sv}}{r} \right) = 0 \quad (1.17)$$

The accurate solution (integration from $\infty$ to $r_s$) of Eq. (1.17) (with the assumption $\Delta h_{sv} \neq f(r)$) is:

$$\ln \left( \frac{T}{T_0} \right) = -\frac{\nu_\gamma}{\Delta h_{sv}} \left( \frac{2\gamma_{sv}}{r_s} \right) \quad (1.18)$$

Solving Eq. (1.18) by a Taylor series of the logarithm accurate to 1st order results in:

$$\frac{\Delta T}{T_0} = \frac{T - T_0}{T_0} = -\frac{\nu_\gamma}{\Delta h_{sv}} \left( \frac{2\gamma_{sv}}{r_s} \right) \quad (1.19)$$
The equilibrium condition of a solid and a liquid particle of identical mass in vacuum can be derived simply by combining the liquid / gas system with the solid / gas system by subtracting Eq. (1.10) from Eq. (1.17), resulting in:

$$\left(\frac{\Delta h_{sl}}{T}\right) dT + \nu_i d\left(\frac{2\gamma_{lv}}{r}\right) - \left(\frac{\Delta h_{lv}}{T}\right) dT + \nu_i d\left(\frac{2\gamma_{lv}}{r}\right) = 0$$  \hspace{1cm} (1.20)

Using the latent heat of melting, \(\Delta h_{sl}\) which is defined as \(\Delta h_{sl} = T(s_f - s_i)\) and the same integration limits as before, the Eq. (1.20) results in:

$$\int_{r_0}^{r} \left(\frac{\Delta h_{sl}}{T}\right) dT + \int_{\infty}^{r} d\left(\nu_i \frac{2\gamma_{lv}}{r}\right) - \int_{\infty}^{r} d\left(\nu_i \frac{2\gamma_{lv}}{r}\right) = 0$$  \hspace{1cm} (1.21)

In the case of melting \(T_0\) is the melting temperature, \(T_M\), of the bulk solid.

The exact solution of Eq. (1.21) and assuming \(m_s = m_i\) and \(h_{sl} \neq f(r)\) is:

$$\ln \left(\frac{T}{T_M}\right) = -\frac{2}{\rho, \Delta h_{lv}} \left(\gamma_{lv} - \gamma_{li} \left(\frac{\rho_s}{\rho_i}\right)^{2/3}\right)$$  \hspace{1cm} (1.22)

which is called the Semenchenko equation.

Solving Eq. (1.22) by a Taylor series of the logarithm accurate to 1st order Eq. (1.22) results in the Pawlow equation:

$$1 - \frac{T}{T_M} = \frac{2}{\rho \Delta h_{lv}} \left(\gamma_{lv} - \gamma_{li} \left(\frac{\rho_s}{\rho_i}\right)^{2/3}\right)$$  \hspace{1cm} (1.23)

The work of Kofman et al. (1994) investigated the surface melting of spherical and non-spherical nanometric lead inclusions and proved experimentally the existence of a liquid layer below the melting temperature at the surface of the inclusions whose thickness is much larger than that observed on the bulk (zero curvature). The proposed phenomenological model is based on the minimization of the Gibbs free energy in equilibrium and shows good agreement with the experimental results, therefore the derivation of Kofman et al. (1994) is discussed.
In a first approach Kofman et al. (1994) showed the existence of surface melting for surfaces with no curvature. Figure 1.2 shows the two possible configurations of a solid with a flat surface in contact with a fluid at the melting temperature. In configuration (1) the solid is in contact with vacuum or its vapor whereas in configuration (2) the solid is in contact with its liquid melt. The liquid wets the solid well. He defines the change in surface energy between configurations (1) and (2) as:

\[ S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) \]  

(1.24)

where \( \gamma \) are the surface tensions (s = solid, l = liquid and v = vapour). Because the liquid wets the solid, configuration 2 is energetically favoured and S is positive.

![Fig. 1.3: The two configurations: solid / external medium with (2) or without (1) an intermediate liquid layer (Fig. 10 of Kofman et al., 1994).](image)

The Gibbs free energy of configuration (1) at constant pressure and temperature is:

\[ G_1 = N\mu_s + A\gamma_{sv} \]  

(1.25)

where \( A, \mu_s \) and \( N \) is the free surface area, the chemical potential of the solid phase and the number of atoms of the solid.

In configuration (2), \( N' \) atoms are in the liquid state. Neglecting the volume change, the Gibbs free energy is:

\[ G_2 = (N - N')\mu_s + N'\mu_l + A\Gamma \]  

(1.26)
where \( \Gamma \) depends on the thickness \( \delta \) of the liquid layer. For \( \delta = 0 \), \( \Gamma = \gamma_{sv} \) and \( \Gamma = \gamma_{sl} + \gamma_{lv} \) if the layer is a bulk liquid. For thin liquid layers the value \( \Gamma \) is an intermediate value which accounts for the interactions between the two layers.

\[
\Gamma = \gamma_{sl} + \gamma_{lv} + S e^{-\delta/\xi}
\]  
(1.27)

where \( \xi \) is the characteristic length describing the short range interactions in liquid metals.

The system equilibrium is obtained by the minimization of \( \Delta G = G_2 - G_1 \)

\[
\frac{\partial (\Delta G)}{\partial \delta} = 0 = \frac{\partial}{\partial \delta} \left( N^i(\mu_i - \mu_s) + AS \left( e^{(-\delta/\xi)} - 1 \right) \right)
\]  
(1.28)

Using the approximation (close to the melting temperature \( T_M \)):

\[
N^i(\mu_i - \mu_s) = V \rho_l \Delta h_b (\Delta T / T_M)
\]  
(1.29)

where \( V = A \delta \) is the volume of the melted layer, \( \rho_l \) the density of the liquid and \( \Delta T = T_M - T \).

\[
0 = \rho_l \Delta h_b \frac{\Delta T}{T_M} - \frac{S}{\xi} e^{(-\delta/\xi)}
\]  
(1.30)

The liquid layer thickness \( \delta \) in equilibrium at temperature \( T \) is given by:

\[
\delta = \xi \ln \left( \frac{S}{\xi \rho_l \Delta h_b (\Delta T / T_M)} \right)
\]  
(1.31)
References


