

# Thermodynamics of nanoparticles

## *Termodinamika nanodelcev*

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**Abstract:** This article deals with the basis for thermodynamic calculations of nanoparticles. Thermodynamics on the nanoscale are different than in bulk form, as there are more surface atoms with surface energy, which is different from bulk atom energy. This contribution of surface energy in nanoparticles changes the mechanisms of melting, grain growth, etc. compared to bulk materials. Using this starting point, one can use these calculations as a basis in nanoparticle synthesis processes. In our research we have synthesized nanoparticles with the process known as Ultrasonic Spray Pyrolysis. This is a versatile process, capable of producing nanoparticles from various materials such as gold, silver, titanium dioxide, nickel, nickel titanium, and so on.

**Key words:** thermodynamics of small systems, nanothermodynamics basics.

**Povzetek:** V prispevku so opisane osnove termodinamičnih preračunov pri obravnavanju nanodelcev. Termodinamika na nivoju nanodelcev se razlikuje od klasične zaradi večjega števila površinskih atomov s površinsko energijo. Ta prispevek površinske energije spremeni mehanizme taljenja, rasti zrn, itd. v primerjavi s sistemi z manjšim deležem površinskih atomov. Ta preračun se lahko uporabi kot začetna točka preračuna pri procesih za sintezo nanodelcev. V našem dosedanjem raziskovalnem delu smo ustvarili nanodelce s procesom, imenovanim ultrazvočna razpršilna piroliza. To je večstranski proces, s katerim je možno proizvesti nanodelce iz več različnih materialov, kot je zlato, srebro, titanov dioksid, nikelj, itn.

**Ključne besede:** termodinamika majhnih sistemov, osnove nanotermodinamike.

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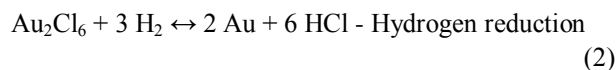
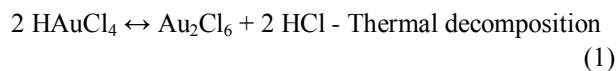
## 1. Ultrasonic spray pyrolysis

Nanoparticles have recently received a lot of attention from the scientific community. The properties of nanoparticles of a material differ from the properties of the bulk material, which gives them a great potential in numerous applications, from electronics to chemistry, biology and medicine. The synthesis of nanoparticles is divided firstly into two groups, top-down and bottom-up methods. In top-down methods, nanoparticles are acquired from a bulkier piece of material, while in bottom-up methods the nanoparticles are built by joining atoms or smaller particles together. Ultrasonic Spray Pyrolysis is a bottom-up method of nanoparticle production. For this process the desired material for nanoparticles must first be dissolved in a precursor solution in low concentrations. The precursor solution is then atomized into micron-sized droplets via ultrasound. These droplets are carried into a furnace by a carrier gas. Inside the furnace the droplets evaporate, leaving only the dissolved material, which is then formed into nanoparticles via the high temperatures and reactions with other gases (reduction or oxidation, depending on the materials used). The final particles are then collected in an appropriate collection system [1–4].

Ultrasonic Spray Pyrolysis can be used for a variety of precursor solutions, producing nanoscaled particles from many different materials, from metal oxides and sulfides, to pure metallic particles, nanocomposites, semiconductor, carbon particles and others [5].

Even though Ultrasonic Spray Pyrolysis (USP) is well known in literature, the actual process mechanisms are understood only theoretically, as it is difficult to observe nanoparticle formation while the synthesis process is under way.

An example of nanoparticle synthesis with USP is the production of gold nanoparticles, using tetrachloroauric acid as the precursor solution. The growth of the nanoparticles takes place in the furnace, where the following equations for particle formation take place:



Even though the process is used for production of nanoparticles from a variety of materials, the basic mechanisms of production are the same for all materials, while the nanoparticle formation is not. This article will try to explain the fundamentals of the reactions in this production process. When the solvent evaporates from the droplet, ideally only the un-reacted form of the desired material is left. After the reactions with the reaction gas inside the furnace, a final particle is formed. However, conventional thermodynamics need to be modified before they are applied to such

small systems. In small systems it should be expected that ordinary thermodynamic principles will not be suitable, as they deal ordinarily with macroscopic systems, where there is a great number of molecules, atoms, ions, etc. [6]. The size of the small systems affects various intensive properties of the system [7]. Experimental work done on small systems is not on a single system, but on a higher number of small systems. For an appropriate accuracy the small systems should not interact with one another and molecular exchanges between the system and the reservoir are no longer negligible, as is the case in macroscopic systems [7]. Nanothermodynamics deals with systems of finite particles, or so called nanophases [8].

Ordinarily, thermodynamics deal with the mean values of extensive quantities as the differences from the mean values are negligible in macroscopic systems. In smaller systems these differences become larger and standard mean values cannot be applied [7]. In regard to this, the melting point of nanoparticles is investigated in this paper from a theoretical standpoint, as others have already dealt with this issue in depth [9–13].

Conventional thermodynamics use well-established methods for investigation of materials. Some approaches for investigations of small systems are surface thermodynamics, computer simulations, statistical mechanics, and Hill's approach based on the concept of sub-divisional potential [14]. The sub-divisional potential is shortly addressed in this paper.

## 2. Chemical potential of small system (nanoparticles)

Small systems are well described by the chemical potential. In a thermodynamic system, chemical potential  $\mu$  is the amount of energy absorbed or released per unit mole ( $\mu$ ), if particles are introduced or removed (here we assume a fixed entropy and volume of a homogeneous system), we can write  $dU = \mu dN$ . For a multiphase system, the change in internal energy is written as:

$$dU = TdS - pdV + \sum_{i=1}^n \mu_i dN_i \quad (3)$$

Here, the changes in volume and entropy are also considered ( $dN_i$  [mass(g)/molar mass (g/mol)]).

Another term is added for small systems, accounting for different energies of molecules at the interfaces, compared to bulk molecules. The energy of surface molecules has to be proportional to changes in the interfacial or surface area,  $d\Sigma$ :

$$dU = TdS - pdV + \sum_{i=1}^n \mu_i dN_i + \gamma d\Sigma \quad (4)$$

The chemical potential can be redefined as:

$$\mu \equiv \mu_{=} + \mu_{\Sigma} \quad (5)$$

Where  $\mu_\infty$  and  $\mu_\Sigma$  are bulk and surface chemical potentials. The interfacial energy  $\gamma$  is also known as surface tension. The size dependent chemical potential for a spherical system can be expressed from the following equations [8]:

$$\mu_\Sigma \equiv \gamma \frac{d\Sigma}{dN} \quad (6)$$

$$d\Sigma = d(4\pi r^2) = 8\pi r dr \quad (7)$$

$$dN = \frac{4\pi r^2}{V_m} dr \quad (8)$$

Where  $V_m$  is the molar volume (the volume of one mole of a substance) of the treated spherical system and  $r$  the sphere radius. After substitution of equations (7) and (8) into equation (6), the surface chemical potential  $\mu_\Sigma$  can be expressed as:

$$\mu_\Sigma = \frac{2\gamma V_m}{r} \quad (9)$$

The chemical potential for a spherical system is then [8]:

$$\mu = \mu_{sphere} = \mu_\infty + \mu_\Sigma = \mu_\infty + \frac{2\gamma V_m}{r} \quad (10)$$

By increasing the sphere radius, the chemical potential of small systems approaches the bulk chemical potential:

$$\mu = \mu_{sphere} \xrightarrow{r \rightarrow \infty} \mu_\infty \quad (11)$$

The term  $\frac{2\gamma}{r}$  is known as the Laplace pressure  $\Delta P$ . The surface chemical potential  $\mu_\Sigma$  of a molar spherical particle is the product of Laplace pressure and molar volume  $\mu_\Sigma = \frac{2\gamma V_m}{r}$ .

### 3. Melting point in small systems

Melting can be presented as a two phase system with a homogeneous solid subsystem ( $\mu_s$ ) and a homogeneous liquid subsystem ( $\mu_l$ ). At the melting point  $T_m$  we can write:

$$\mu_s = \mu_{s,\infty} + \frac{2\gamma V_m}{r} = \mu_l \quad (12)$$

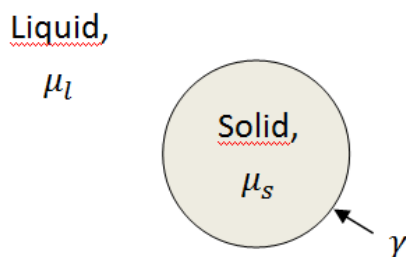


Figure 1. Two phase system at melting point  $T_m$ .

The equation (12) can be expanded with a small temperature difference  $\Delta T$  between the bulk melting temperature  $T_{m,\infty}$  and the particle temperature  $T(r)$ :

$$T(r) + \Delta T = T_{m,\infty} \quad (13)$$

$$\begin{aligned} \mu(p, T_{m,\infty} - \Delta T) &= \mu(p, T_{m,\infty}) + \int_{T_{m,\infty}}^{T_{m,\infty} - \Delta T} \left(\frac{\partial \mu}{\partial T}\right)_p dT = \\ &= \mu(p, T_{m,\infty}) - \int_{T_{m,\infty}}^{T_{m,\infty} - \Delta T} S_m dT \end{aligned} \quad (14)$$

The molar entropy  $S_m$  is introduced in the previous expression as a substitute for the following Maxwell relation [7], [14], [15]:

$$-\left(\frac{\partial S}{\partial N}\right)_p = \left(\frac{\partial \mu}{\partial T}\right)_p \quad (15)$$

$$S_m = \left(\frac{\partial S}{\partial N}\right)_p, \quad S_m = -\left(\frac{\partial \mu}{\partial T}\right)_p \quad (16)$$

The solid and liquid phase can be expressed as:

$$\begin{aligned} \mu_s(p, T_{m,\infty} - \Delta T) &= \mu_{s,\infty}(p, T_{m,\infty}) - \\ &- \int_{T_{m,\infty}}^{T_{m,\infty} - \Delta T} S_{m,s} dT + \frac{2\gamma V_m}{r} \end{aligned} \quad (17)$$

$$\mu_l(p, T_{m,\infty} - \Delta T) = \mu_{l,\infty}(p, T_{m,\infty}) - \int_{T_{m,\infty}}^{T_{m,\infty} - \Delta T} S_{m,l} dT \quad (18)$$

At the equilibrium temperature  $T_m$ ,  $\mu_s = \mu_l$ :

$$\int_{T_{m,\infty}}^{T_{m,\infty} - \Delta T} (S_{m,l} - S_{m,s}) dT + \frac{2\gamma V_m}{r} = 0 \quad (19)$$

The molar entropy difference of the liquid and solid phase of our small system (“entropy of fusion”) can be replaced with the enthalpy of fusion:

$$\Delta S = S_{m,l} - S_{m,s} \approx \Delta H_f / T \quad (20)$$

The enthalpy of fusion is the change in enthalpy resulting from heating a substance to change its state from a solid to a liquid. This change of states occurs at the melting point temperature.

When we are considering the entropy difference of the liquid and solid phase ( $S_{m,l} - S_{m,s}$ ), we are assuming small differences when the phase change occurs, as entropy is a function of combined contributions of the individual atoms. With small systems there is smaller number of atoms and a higher number of surface atoms (a higher surface-to-volume ratio), resulting in a smaller combined entropy difference when the phase change occurs. It was shown, that extremely small systems possess the lowest entropy of fusion. With a particle of diameter of 2.5 nm or less, all of the atoms are subdued to surface effects and the entropy of fusion is expected to vanish [16].

The phase change entropy difference can be translated to the enthalpy of fusion  $\Delta H_f$  for which we will assume that it does not change very much with very

small temperature changes. As such, we can assume  $\Delta H_f$  to be constant. Substituting equation (20) into equation (19) and including the assumption of a constant  $\Delta H_f$ , we can write:

$$\Delta H_f \int_{T_{m,\infty}}^{T_{m,\infty}-\Delta T} \frac{1}{T} dT + \frac{2\gamma V_m}{r} = \Delta H_f \ln\left(1 - \frac{\Delta T}{T_{m,\infty}}\right) + \frac{2\gamma V_m}{r} = 0 \quad (21)$$

At small temperature changes  $\Delta T$ , the expression  $\ln\left(1 - \frac{\Delta T}{T_{m,\infty}}\right)$  is approximately equal to  $\frac{T(r)}{T_{m,\infty}} - 1$ . The melting temperature can then be expressed as:

$$T(r) = T_{m,\infty} \left(1 - \frac{2\gamma V_m}{\Delta H_f r}\right) \quad (22)$$

This expression is a form of the Gibbs-Thomson equation for spherical particles [9]. The calculated melting temperatures of gold nanoparticles with equation (22) are presented in Figure 2. The bulk melting point for gold is 1064.18°C.

According to this theory, as seen in Figure 2, very small particles have a very low melting point in

comparison to larger ones. The enthalpy of fusion is assumed to be a constant (equation (20)), as we have addressed only small temperature differences  $\Delta T$ . This may be acceptable for larger particles; however, for smaller particles there seem to be discrepancies, as the enthalpy of fusion is decreasing for very small particles. It was hypothesized, that there is a critical particle size, where the properties of the liquid and solid are indistinguishable, causing the enthalpy of fusion to become zero [9]. For extremely small sizes, such as a few nanometers, the chart in Figure 2 should be addressed separately. However, for the sizes produced with the USP process these calculations should be adequate, as our produced nanoparticle sizes are usually larger (more than 10-20 nm) [2], [3]. The USP process also prevents the production of extremely small gold nanoparticles as it needs to be performed at a certain temperature for thermal decomposition (equation (1)) to occur (around 300°C for gold), in order to synthesize nanoparticles.

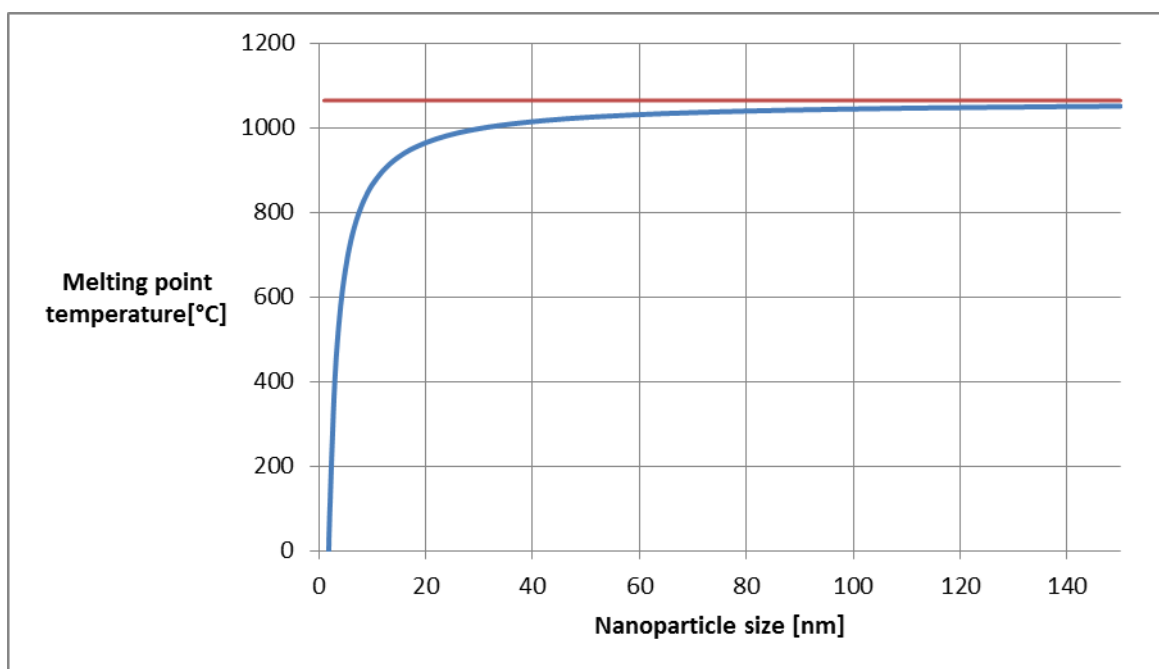


Figure 2. Melting point of different sizes of gold nanoparticles.

#### 4. Phase transformations in small systems

Phase transformations change the state and free energy of a system. The change in free energy is the driving force for phase transformations. The Gibbs free energy is defined as

$$G = U + pV - TS = H - TS \quad (23)$$

Where  $G$  denotes Gibbs free energy,  $U$  – internal energy,  $p$  – pressure,  $V$  – volume,  $T$  – temperature,  $S$  – entropy of the system. Enthalpy  $H$  is the combination of  $U + pV$ .

##### 4.1. Small systems with $\mu$ , $V$ , $T$

For an example of a one-component system of a spherical particle with a volume  $V$ , at chemical potential  $\mu$  in a reservoir with temperature  $T$  and mean pressure  $p$ , we cannot assume that usual thermodynamic equations are valid:

$$dU = TdS - pdV + \mu dN \quad (24)$$

The size of the system must be taken into account and another parameter is introduced:  $\mathcal{N}$  – the number of small systems, each with a fixed center of mass, and with properties of  $\mu$ ,  $V$  and  $T$ . If  $\mathcal{N} \rightarrow \infty$ , accounting for a great number of small systems, then we are dealing with a macroscopic thermodynamic system, no matter the sizes of single systems. The individual systems' fixed center of mass eliminates translational degrees of freedom of the whole system. For a number of small systems  $\mathcal{N}$ , for the total ensemble of systems, we have:

$$dU_T = TdS_T - pNdV + \mu dN_T \quad (25)$$

Subscript T = total, relating to the properties of the entire number of small systems together. The expression can be expanded, as  $U_T$  is also a function of  $\mathcal{N}$ .

$$dU_T = TdS_T - pNdV + \mu dN_T + Xd\mathcal{N} \quad (26)$$

$$X = (\partial U_T / \partial \mathcal{N})_{S_T, V_T, N_T} \text{ or } -X/T = (\partial S_T / \partial \mathcal{N})_{U_T, V_T, N_T} \quad (27)$$

$X$  is a sort of “system chemical potential” of the entire ensemble of small systems. It is called the subdivision potential [14].

When  $\mu$ ,  $V$  and  $T$  are constant and only  $\mathcal{N}$  changes, then  $U_T$ ,  $S_T$  and  $N_T$  change according to  $\mathcal{N}$ .  $U_T$  is a linear homogeneous function of  $S_T$ ,  $N_T$  and  $\mathcal{N}$ .

$$U_T = TS_T + \mu N_T + X\mathcal{N} \quad (28)$$

$$U_T = \mathcal{N}\bar{U} \quad (29)$$

$$N_T = \mathcal{N}\bar{N} \quad (30)$$

$$S_T = \mathcal{N}S \quad (31)$$

$\bar{U}$  and  $\bar{N}$  are average values per small system, as they fluctuate according to  $\mu$ ,  $V$  and  $T$  of single small systems.  $S$  does not fluctuate in value and is the same

for each system. Expressing  $X$  from equation (27), we now obtain:

$$X\mathcal{N} = \mathcal{N}\bar{U} - TS - \mu\mathcal{N}\bar{N} \quad (32)$$

Divided by  $\mathcal{N}$ , we obtain the expression for a single small system:

$$X = \bar{U} - TS - \mu\bar{N} \quad (33)$$

We define  $X \equiv -\bar{p}V$ ,  $\bar{p}$  is an “integral” pressure, i.e. a pressure for a single system, different from  $p$  which is a “differential” pressure, applicable to the ensemble of systems [7]. Thus we can write  $\bar{U}$  for the single small system as:

$$\bar{U} = TS - \bar{p}V + \mu\bar{N} \quad (34)$$

If we now address the ensemble of systems as a single system in analogue to equation (23), we obtain:

$$d\bar{U} = TdS - \bar{p}dV + \mu d\bar{N} \quad (35)$$

If equation (34) is integrated, the expression  $X$  cannot be re-obtained. This means that  $\bar{U}$  is not a linear homogeneous function of  $S$ ,  $V$  and  $\bar{N}$ , in agreement with the assumption that usual thermodynamic equations are not valid for small systems in equation (23):

$$\bar{U} \neq TS - \bar{p}V + \mu\bar{N} \quad (36)$$

Several small systems can be treated in the same way. In this instance we have addressed a small system with a volume  $V$ , at chemical potential  $\mu$  in a reservoir with temperature  $T$ . The same principals can be used with a system with known  $p$ ,  $N$ ,  $T$ , or a system with constant  $N$ ,  $V$  and  $T$ , etc.

##### 4.2. Small systems in general

A more general approach applicable to all environments is possible, where we add systems to the entire ensemble for any environment. Thus we have:

$$U_T = \mathcal{N}U \quad (37)$$

$$N_T = \mathcal{N}N \quad (38)$$

$$V_T = \mathcal{N}V \quad (39)$$

$$S_T = \mathcal{N}S \quad (40)$$

From here we obtain:

$$dU_T = TdS_T - p dV_T + \mu dN_T + \mathcal{E}d\mathcal{N} \quad (41)$$

With  $\mathcal{E}$  defined as:

$$\mathcal{E} \equiv (\partial U_T / \partial \mathcal{N})_{S_T, V_T, N_T} \quad (42)$$

Alternatively we can obtain:

$$dS_T = \left(\frac{1}{T}\right) dU_T + \left(\frac{p}{T}\right) dV_T - \left(\frac{\mu}{T}\right) dN_T + \mathcal{S}d\mathcal{N} \quad (43)$$

Where we define  $\mathcal{S}$ :

$$\mathcal{S} \equiv (\partial S_T / \partial \mathcal{N})_{U_T, V_T, N_T} \quad (44)$$

$$\mathcal{S} = -\mathcal{E}/T \quad (45)$$

With the definition of  $\mathcal{E}$ , more systems are added, increasing  $\mathcal{N}$  and holding  $U_T, V_T$  and  $N_T$  constant. This means that  $U, V$  and  $N$  are decreasing, as  $\mathcal{N}$  increases. The systems are being divided into smaller systems and retaining the same total energy, volume and number of molecules. After integration:

$$U_T = TS_T - pV_T + \mu N_T + \mathcal{E}\mathcal{N} \quad (46)$$

$$U = TS - pV + \mu N + \mathcal{E} \quad (47)$$

$$S = \left(\frac{1}{T}\right)U + \left(\frac{p}{T}\right)V - \left(\frac{\mu}{T}\right)N + \mathcal{S} \quad (48)$$

$$dU = TdS - pdV + \mu dN \quad (49)$$

$$\mathcal{E} = -SdT - Vdp - Nd\mu \quad (50)$$

$$d\mathcal{S} = -Ud\left(\frac{1}{T}\right) - Vd\left(\frac{p}{T}\right) + Nd\left(\frac{\mu}{T}\right) \quad (51)$$

For a macroscopic system,  $\mathcal{E}$  and  $\mathcal{S}$  disappear. These equations can be used for all examples, for instance, if the environmental variables are  $\mu, V$  and  $T$ , the following equation is relevant [7]:

$$d(\mathcal{E} - pV) = -SdT - pdV - Nd\mu \quad (52)$$

And  $\mathcal{E} = (p - \bar{p})V$ . This equation is applicable when the environmental variables are  $\mu, V$  and  $T$ . The general approach can be also used to obtain formulations when the variables are  $p, N, T$ , or  $N, V$  and  $T$ , and so on.

## 5. Conclusion

Some basics for thermodynamic calculations in regards to small systems have been presented. Some expressions have been added to standard bulk thermodynamic equations. The melting point of small particles was addressed in connection with the USP process. For extremely small particles, the proposed melting point model cannot be applied. However, it was found to be adequate for the USP process as generally larger particles are synthesized with USP. Hill's small systems approach to thermodynamics was shown with an example for an ensemble of small systems with  $\mu, V$  and  $T$  as constants, with an added general approach for the treatment of small systems. These expressions correct the standard bulk equations of thermodynamics and can be used as a basis for further treatment of small systems with specific parameters.

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