Advances in thermodynamic modelling of nanoparticles

Grégory Guisbiers

Department of Physics & Astronomy, University of Arkansas at Little Rock, Little Rock, AR, USA

ABSTRACT
Among all the computational techniques (Density Functional Theory, Molecular Dynamics, Monte-Carlo Simulations, Nanothermodynamics) used to investigate the properties of nanoparticles, nanothermodynamics is the most unusual one. Indeed, most people still think that thermodynamics does not apply at the nanoscale; nonetheless, thermodynamic concepts can still be applied at the nanoscale to predict various properties of nanoparticles like melting temperature, energy bandgap... In this review, we first introduce the fundamental concepts and methods of nanothermodynamics starting from Hill's contributions to the most recent developments focusing specifically on the relationship between the material property and the following parameters as quantum statistics (Fermi-Dirac or Bose-Einstein), size and shape of the nanoparticle.

1. Introduction
The concept of ‘nanotechnology’ was first introduced to the world on 29 December 1959 by the theoretical physicist Richard Feynman (1918–1988) during his famous lecture ‘There is plenty of room at the bottom’ at the annual American Physical Society meeting at Caltech [1]. However, the invention of scanning probe microscope and the discovery of C₆₀ fullerenes were still two decades away. The plenty of room, Feynman was referring to,
came from electron microscopy observations that allowed scientists in 1959 to observe details as small as \(~1\) nm; but that resolution limit was still too large to observe atoms individually [2]. The major problem of electron microscopy at that time was spherical aberration [3], a problem solved in the late 1990s with the presence of quadrupoles and octopoles in aberration-corrected electron microscopes [4].

During the same period, another theoretical physicist, Terrell L. Hill (1917–2014), presented a brief introduction of his work on the thermodynamics of small systems at the American Chemical Society meeting at Washington D. C. on 23 March 1962 [5] and he published a first paper on that topic the exact same year in the Journal of Chemical Physics [6]. Then, he refined his ideas and finally published his famous book ‘Thermodynamics of Small Systems’ in 1964 [7]. Thermodynamics is all about conservation of energy (1st law of thermodynamics) and as everybody knows it is always true. So, this theory should still be applicable at the nanoscale. His main idea was that the size of a system affects various intensive properties of that system and this modification should be considered into the conservation of energy. His work stayed mostly unknown during 40 years; it is only when Paul Alivisatos, one of the two Editors-in-chief of the freshly launched ‘Nano Letters’ journal (established in January 2001 by the American Chemical Society), invited him to write a paper in the first volume of ‘Nano Letters’ that the scientific community became fully aware of his work [8]. Indeed, the progress in the synthesis and processing of nanomaterials has created the demand for greater scientific understanding of the thermodynamics at the nanoscale. This review paper summarizes the advances made by different thermodynamics group around the world to the field of nanotechnology.

2. Hill’s theory

A first approach to discuss the thermodynamics of small systems is by introducing the finite size effects within the macroscopic thermodynamics (Table 1). Hill did that by introducing a new thermodynamic potential called the sub-division potential, $U_{sub}$, and it is defined as [6–8]:

$$U_{sub} = \left( \frac{\partial U}{\partial N_{sub}} \right)_{S,V,N}$$

(1)

where $U$ is the internal energy of the system, $S$ is the entropy of the system, $V$ is the volume of the system, $N$ is the number of particles within the system and $N_{sub}$ is the number of sub-divisions in the system. Therefore, at the nanoscale, the internal energy of the system made of a single component material, $U$, is given by the Euler’s equation:
where the temperature, $T$, and entropy, $S$, are the thermal conjugate variables; the pressure, $p$, and volume, $V$, are the mechanical conjugate variables; the chemical potential, $\mu$, and the number of particles, $N$, are the chemical conjugate variables. There exist a new pair of conjugate variables at the nanoscale ($U_{sub}, N_{sub}$) represented by the sub-division potential and the number of sub-divisions. Generally, the number of sub-divisions is much smaller than the number of particles in the system ($N_{sub} < N$) \[9\].

Therefore, the Gibbs free energy of the system at the nanoscale, $G$, becomes;

$$G = \mu N + U_{sub}N_{sub}$$ \hspace{1cm} (3)

Equation (3) is often generally simply written as the summation between two contributions, the bulk and the surface ones as $G = G_\infty + G_\Sigma$ where $G_\infty = \mu N$ (extensive term) and $G_\Sigma = U_{sub}N_{sub}$ (non-extensive term) \[10,11\]. At the bulk scale, the chemical potential is simply given by $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} = \left(\frac{\partial U}{\partial N}\right)_{S,V} \equiv \mu_\infty$ while at the nanoscale the chemical potential becomes $\mu = \mu_\infty + \frac{\partial U_{sub}}{\partial N} N_{sub}$ \[12,13\]. Thus, $\mu$ is a function of just two independent variables $T$ and $p$. However, since the extensive state functions of nanoparticles are not linearly proportional to $N$, $\mu$ is not just a function of $T$ and $p$, but is also a function of $N$. Hill’s sub-division potential, $U_{sub}$, can be understood by comparison to Gibbs’ chemical potential, $\mu$. $\mu$ is the change in energy to take a single particle from a bath of particles into the system, whereas $U_{sub}$ is the change in energy to take a cluster of $N$ interacting particles from a bath of clusters into the system \[14,15\].

### 3. Tsallis’ theory

The second approach to discuss the thermodynamics of small systems is to consider their non-extensivity by redefining the entropy (Tsallis’ approach) instead of redefining the internal energy (Hill’s approach). Indeed, when a physical quantity $\chi$ is expressed by $\chi \propto N^\lambda$, they are classified into two groups: intensive ($\lambda = 0$) and extensive ones ($\lambda = 1$). A physical quantity is intensive if it is invariant under changes to the system size ($\lambda = 0$).
A physical quantity is extensive if it scales linearly with the system size \((\lambda = 1)\). We shall refer to \(\lambda\) as Euler exponent as it is defined through Euler’s theorem of homogeneous functions: \(\chi(\lambda x, \lambda y, \lambda z) = \lambda \chi(x, y, z)\) [16]. By shrinking the size of a system to the nanoscale, its surface-to-volume ratio varies as \(N^{-1/3}\) [17–19], meaning that \(\lambda\) is neither 0 nor 1, therefore the system behaves non-extensively (Table 1). When the surface to volume ratio increases the non-extensivity becomes more pronounced. And consequently, non-extensivity is described by a fractal Euler exponent, \(\lambda\).

The task of redefining the entropy was undergone in 1988 by Constantino Tsallis (1943-) and this non-additive entropy, \(S_q\), is known today as the Tsallis’ entropy [20–23]:

\[
S_q = \frac{k}{1-q} \left( \sum_{i=1}^{\Omega} p_i^q - 1 \right) = k \ln_q \Omega
\]

where the \(q\)-logarithm is defined as \(\ln_q \zeta = \frac{\zeta^{1-q} - 1}{1-q} (\zeta > 0 \text{ and } \ln_1 \zeta = \ln \zeta)\); \(\Omega\) is the total number of microstates; \(p_i\) is the probability of finding the system in the \(i^{th}\) microstate (with the condition that \(\sum_{i=1}^{\Omega} p_i = 1\)); \(q\) is the entropic index, a real parameter which characterizes the degree of non-additivity of the entropy (i.e. a measure of how strong the correlations are) and \(k\) is the Boltzmann’s constant \((k_B)\) when \(q = 1\) otherwise \(k \neq k_B\) when \(q \neq 1\).

If a system has weak or no correlations at all, then the number of microstates \(\Omega\) increases exponentially with the number of elements \(N\) i.e. \(\Omega = X^N\), and the non-additive entropy \(S_q\) is extensive for \(q = 1\) \((S_{q=1} = kN \ln X)\) and non-extensive for all \(q \neq 1\). Whereas, if the system has strong correlations, the number of microstates \(\Omega\) increases and can be described by a power law, \(\Omega = N^X\). The non-additive entropy \(S_q\) is therefore extensive for \(q = 1 - \frac{1}{X}\) while being non-extensive for all other values of \(q\), including \(q = 1\) \((S_{q=1} = kX \ln N)\).

By using Penrose’s definition of entropic additivity (Equation (5)), we have that the entropy \(S_q\) is non-additive for all values of \(q\) except for \(q = 1\). Indeed, when \(q = 1\), the entropy is additive and the usual Boltzmann–Gibbs entropy is recovered \((S_{q=1} = k \ln \Omega)\) [24].

\[
S_q(A + B) = S_q(A) + S_q(B) + \frac{1-q}{k} S_q(A)S_q(B)
\]

Where \(A\) and \(B\) are two independent systems. The case \(q < 1\), \(q = 1\), \(q > 1\) correspond, respectively, to super-extensivity, extensivity and sub-extensivity.

The Hill’s approach can be deduced from the Tsallis formalism by defining the sub-division potential as [9,13,25,26]:
The non-additivity property of the Tsallis entropy forms the basis of the non-extensivity of the sub-division potential.

4. Thermodynamic limit

The question ‘Small systems: when does thermodynamic apply?’ was raised 80 years ago in the context of world war II during the development of nuclear weapons [27]; at that time, Weisskopf, Landau and Frenkel were introducing the concept of temperature in nuclear reactions. Nowadays, within the context of nanotechnology, this question has to be asked again [9,28]! The thermodynamic limit is essentially a consequence of the law of large numbers, i.e. when sample size tends to infinity, the sample mean equals to population mean. Consequently, the ratio of the size of the fluctuations to the mean is of order \( \frac{\delta N}{N} : \frac{1}{\sqrt{N}} \) meaning that the fluctuations vanish when the system becomes macroscopic or the fluctuations become huge at small scales (Table 1).

At the macroscale, the Euler’s equation is \( U - TS + pV - \mu N = 0 \); and consequently, the temperature is defined as the partial derivative of the internal energy with respect to the entropy:

\[
T = \left( \frac{\partial U}{\partial S} \right)_{S,V,N} \tag{7}
\]

However, at the nanoscale the Euler’s equation becomes \( U - TS + pV - \mu N = U_{\text{sub}}N_{\text{sub}} \), therefore the temperature is redefined by the following expression:

\[
T = \left( \frac{\partial U}{\partial S} \right)_{S,V,N} - \left( \frac{\partial U_{\text{sub}}}{\partial S} \right)_{S,V,N} N_{\text{sub}} - U_{\text{sub}} \left( \frac{\partial N_{\text{sub}}}{\partial S} \right)_{S,V,N} \tag{8}
\]

Suppose that we have one system that we separate into two identical smaller systems, the decrease in the temperature of the smaller systems can be understood by the conversion of internal energy into surface energy. The decrease of internal energy decreases the kinetic energy of the particles and consequently the temperature. Therefore, to get an idea of the relative temperature fluctuation \( \frac{\delta T}{T} : \frac{1}{\sqrt{N}} \) inside a cube made of 10,000 gold atoms \( (L \sim 3.4 \text{ nm}) \), the fluctuation reaches \( \sim 1\% \) while it reaches \( \sim 10\% \) for a cube made of 100 gold atoms \( (L \sim 0.7 \text{ nm}) \) [27,29,30]. Consequently, there is no strict thermodynamic validity limit at the nanoscale, the limit you want to set only depends on the magnitude of the fluctuation you are ready to accept on the material property you are studying [30–34].
can still be applied at the nanoscale because the temperature can be defined for small systems (Equation (8)) by using either a classical or quantum approach. Indeed, classically, the temperature can be defined from the kinetic energy of particles constituting the system; consequently, the temperature can be defined very locally even for one atom. Quantum-mechanically, the temperature is defined from the quanta of vibrations (phonons); therefore, the temperature can only be defined for sizes larger than the phonon mean free path due to Heisenberg’s principle [35]. As the phonon mean free path is temperature-dependent, the classical definition will differ only from the quantum one at low temperatures [36,37].

5. Fermionic or bosonic material property?

All particles in nature are either bosons or fermions. As a general rule, matter is made of fermions, e.g. protons, neutrons and electrons are fermions. Bosons are particles (quanta) associated with interactions, e.g. photons and phonons are bosons. A fermion is a particle that follows Fermi–Dirac statistics while a boson is a particle that follows Bose-Einstein statistics. Therefore, by having only two types of particles in nature, there will be only two types of size-dependent material properties in nature; the ones that follow a Fermi-Dirac statistics and the others that follow a Bose-Einstein statistics. By analyzing the size-dependency of several different material properties like, for example, the melting temperature, Debye temperature, cohesive energy . . . ; it has been found by Guisbiers [38–40] that all those size-dependent material properties can be described by using only two scaling laws (one fermionic and one bosonic; Figure 1) which can therefore be unified into one single scaling relationship as:

![Figure 1](image_url)

**Figure 1.** Normalized size-dependent material property ($\xi/\xi_\infty$) versus the shape-dependent parameter quantifying the magnitude of the size effect ($\alpha_{shape}$) for different sizes of nanoparticles (D) when material properties follow (a) Fermi-Dirac statistics or (b) Bose-Einstein statistics. The point (0, 1) in both graphs corresponds to the bulk material. The yellow region indicates the region where thermodynamics undergoes significant fluctuations (larger than ~10%). (Adapted with permission from Ref [39]).
\[
\frac{\xi}{\xi_\infty} = \left(1 - \frac{\alpha_{\text{shape}}}{D}\right)^{S^{-1/2}} \tag{9}
\]

where \(\xi\) represents the size/shape-dependent material property and \(\xi_\infty\) represents the bulk material property, \(S\) represents the type of quantum statistics, i.e. the particle obeys to either Fermi-Dirac \((S = 1/2)\) or Bose-Einstein \((S = 1)\). \(\alpha_{\text{shape}}\) is defined as \(\alpha_{\text{shape}} = \left[AD(y_s - y_l) / [V\Delta H_{m,\infty}]\right]\); where \(A/V\) is the surface-to-volume ratio, \(\Delta H_{m,\infty}\) is the bulk melting enthalpy, and \(y_l\) and \(y_s\) are the surface energies in the liquid and solid states, respectively. Physically, \(\alpha_{\text{shape}}\) quantifies the magnitude of the size effect; the values indicated in Figure 2 are for spherical nanoparticles. Values of \(\alpha_{\text{shape}}\) for other polyhedral shapes can be found in Ref \[41\].

From Equation (9), it is clear that for a given material (i.e. a given \(\alpha_{\text{shape}}\) parameter) and a given size \((D)\), the size effect on materials properties described by a Fermi–Dirac statistic (“fermionic properties”) is more pronounced than the size effect on materials properties described by a Bose–Einstein one (“bosonic properties”). Moreover, the scaling exponent in Equation (9) exhibits the fractal nature of size effects, \(S^{-1/2}\) being either a non-integer equal to \(1/2\) or an integer equal to 1. Some phase transitions like order-disorder and superconductivity exhibit a scaling exponent equals to \(1/2\) while others exhibit a scaling exponent equal to 1 like melting. Moreover, Xiong et al. also confirmed that for some physico-chemical properties like the Debye temperature (i.e. temperature of a material’s highest normal mode of vibration) the size-dependency adopts a \(1/2\) scaling exponent following therefore this scaling law \(\xi/\xi_\infty = (1 - \alpha_{\text{shape}}/D)^{1/2}\) [42]. The square root size-dependency of the Debye temperature has also been confirmed by Yang et al. [43]. At frequencies lower than the Debye frequency \((kT_{\text{Debye}} = \hbar\omega_{\text{Debye}})\), it has been recently confirmed...
experimentally that vibrations of nanoparticles are still ruled by continuum mechanics laws down to sizes of a few nanometers \([44,45]\). At frequencies higher than the Debye frequency, the ‘lattice’ is unable to ‘see’ the vibrations because the wavelength of the vibrations is smaller than the lattice parameter; therefore, the vibrations become independent from the lattice.

In conclusion, the universality of 1/D size-dependency has been confirmed by Vanithakumari et al. \([46]\) and Xiong et al. \([42]\) for most physico-chemical properties. Moreover, it is observed that low-temperature phenomena are described by a \(\frac{1}{2}\) scaling exponent while higher temperature phenomena are described by a unitary scaling exponent.

6. Melting temperature of NPs

The solid-liquid phase transition of nanoparticles has been investigated by the scientific community since 1850. Faraday was the first scientist emitting the idea that the melting temperature of nanoparticles should be smaller than the bulk melting temperature. A more detailed discussion concerning the most important theoretical models predicting the size-dependency of the melting temperature can be found in Refs \([17,47,48]\). Based on Equation (9), the size-dependent melting temperature is described by \([49,50]\):

\[
\frac{T_m}{T_{m,\infty}} = 1 - \frac{\alpha_{\text{shape}}}{D}
\]  

(10)

Where \(T_m\) is the melting temperature of the nanoparticle having a size \(D\), \(T_{m,\infty}\) is the bulk melting temperature, \(\alpha_{\text{shape}}\) is the parameter quantifying the magnitude of the size effect and \(D\) is the size of the nanoparticle. Almost all the theoretical models mentioned in Refs \([47,48]\) predict a size dependency as written in Equation (10), only the value of the \(\alpha_{\text{shape}}\) parameter may differ. The 1/D behavior of Equation (10) is illustrated in Figure 3 \([17]\). The 1/D behavior has been recently verified experimentally by heating gold nanoparticles having diameters below 5 nm in-situ a Transmission Electron Microscope (TEM) \([51]\).

By using the fluctuations theory, the thermodynamic correction factor for a single component system is defined based on the fluctuating number of particles within the system \([52]\):

\[
\frac{1}{\Gamma} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}
\]  

(11)

where the brackets denote an ensemble average and \(N\) is the number of particles in the system. Equation (11) can be rewritten in a similar way as Equation (10) \([53,54]\):
where $C$ is a constant related to the surface effect that do not depend on the size $D$ i.e. $C$ is a function of $\alpha_{\text{shape}}$. Therefore, the thermal properties of a small system differs from those of a large system but in a predictable way, $1/D$ [52,55,56].

### 7. Energy bandgap of NPs

The energy bandgap, $E_g$, of a semiconductor can also be predicted by using thermodynamic concepts. Indeed, the energy bandgap can be described as the variation of the Gibbs free energy between the conduction and valence energy bands, namely, $E_g = \Delta H_{cv} - T \Delta S_{cv}$, where $\Delta H_{cv}$ and $\Delta S_{cv}$ are the variation of enthalpy and entropy between the conduction and valence energy bands, respectively [57]. At the nanoscale, the energy bandgap varies with the size of the semiconductor and it increases when the size is reduced. From Equation (9), it is known that any fermionic ($S = 1/2$) property, $\xi$, scales like $\Delta \xi / \xi_\infty = \alpha_{\text{shape}} / D$. Applying the aforementioned fermionic scaling law, $\Delta \xi / \xi_\infty = \alpha_{\text{shape}} / D$, to the energy bandgap and melting temperature, produces $\Delta T_m / T_{m,\infty} = |\Delta E_g / E_{g,\infty}|$ where $T_m$ ($E_g$) and $T_{m,\infty}$ ($E_{g,\infty}$) represent the size-dependent and bulk melting temperature (energy bandgap) of the material, respectively. Consequently, the size-dependent bandgap energy, $E_g$, can be calculated by employing the following scaling law, $E_g / E_{g,\infty} = 2 - T_m / T_{m,\infty}$.
The exact same scaling law was obtained by Li et al. [62] when expressing the size and temperature-dependency of the electrical conductivity as an Arrhenius equation:

\[
\sigma(D, T) = \sigma_0 e^{\frac{Q(D)}{k_B T}}
\]  

(13)

where \(\sigma_0\) denotes a pre-exponential constant, \(Q(D)\) is the size-dependent activation energy for electrical migration within a nanoparticle, \(k_B\) is Boltzmann’s constant and \(T\) is temperature. For intrinsic semiconductors (non-doped), the size-dependent activation energy is related to the size-dependent energy bandgap as \(Q(D) = E_g(D)/2\) [63]. Therefore, the following equality is obtained:

\[
\frac{\Delta E_g}{E_{g,\infty}} = 1 - \frac{Q(D)}{Q_{\infty}}
\]

(14)

At the melting temperature, \(T_m\), the electrical conductivity is assumed to be size-independent meaning that \(\sigma(D, T_m) = \sigma(\infty, T_{m,\infty})\). Therefore, we get

\[
\frac{Q(D)}{Q_{\infty}} = \frac{T_m(D)}{T_{m,\infty}}
\]

(15)

By combining Equations 13 and 14, we obtain the same scaling law, \(E_g/E_{g,\infty} = 2 - T_m/T_{m,\infty}\), as previously obtain when expressing the energy bandgap as \(E_g = \Delta H_{cv} - T\Delta S_{cv}\) [64–66]. On Figure 4, the validity of the scaling law is illustrated on CdS nanoparticles. The exciton Bohr radius of

![Figure 4. Energy bandgap versus the size of CdS nanoparticles. The experimental data come from Refs [116–119]. The following scaling law, \(E_g/E_{g,\infty} = 1 + a_{sphere}/D\), has been used to predict the energy bandgap of CdS nanoparticles at the nanoscale with a parameter \(a_{sphere} = 0.38\) nm [114].](image-url)
CdS is 1.50 nm meaning that at 3 nm the energy bandgap starts being affected by quantum effects [67].

8. Phase diagrams of NPs

At the nanoscale, the range of properties is extended by tuning the size, shape of the system [68,69]; but it can also be extended by taking mixtures of elements to generate alloys [70]. Generally, there is an enhancement in specific properties upon alloying due to synergistic effects [71]. As illustrated in Figure 5, there is a very wide range of combinations and compositions possible for nano-alloys. Four types of mixing patterns (a, b, e, and f) can be identified in Figure 5: core-shell structure, Janus structure, random alloying and ordered alloying. Some variants are possible (c, d, g, h). The fingerprint of an alloy is its phase diagram. A binary phase diagram is a visual representation, at constant pressure, of phases at equilibrium between two elements for any combination of temperature and composition. Obtaining the phase diagrams for binary systems at the nanoscale has been a long-sought goal [72–74]. At the nanoscale, the experimental determination of these phase diagrams is almost impossible because it requires calorimetry measurements which are very challenging to perform because of the small mass involved [75–77]. In this area, theoretical modelling is very often the only tool that can be used to infer the thermodynamics of nano-alloys [78,79]. A list of the known binary phase diagrams at the nanoscale is indicated in Table 2. As it can be seen

![Figure 5](image-url). Patterns exhibited by bimetallic nanoalloys at various temperatures. (a) Solid core/shell; (b) ordered alloy; (c) alloyed core/pure shell; (d) liquid core/shell; (e) Janus-like; (f) random alloy; (g) solid core/liquid shell; (h) alloyed liquid. (Reproduced with permission from Ref [49]).
from Table 2, only 24 binary phase diagrams are known at the nanoscale for various nanoparticle shapes; so, there is still a huge amount of work to do in order to calculate the other 3136 possible binary phase diagrams. Indeed, around ~80 chemical elements from the periodic table are stable; therefore, the number of 2-combinations among 80 elements gives us 3160 binary phase diagrams in total.

Most of the calculated phase diagrams have been obtained at the nanoscale by using nano-thermodynamics (or also called nano-calphad [73]). The Gibbs free energy (GFE) of the alloy within a single phase is given by [80,81]:

\[
G(x_i, T) = \sum_i x_i G_i^0 + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \sum_\nu \Omega_{ij}^\nu (x_i - x_j) \nu
\]  

(16)

where \(x_i\) is the composition in element \(i\), \(G_i^0\) is the GFE of the pure element \(i\), \(R\) is the molar gas constant, and \(T\) is the temperature. \(\Omega_{ij}^\nu\) is the interaction energy for each pair of elements \(ij\), and \(\nu\) is a parameter equal to 0 for regular solutions and 1 for sub-regular ones. In Equation (15), the first two terms represent the Gibbs free energy of ideal mixing while the last term represents the excess Gibbs energy of mixing. The Gibbs energy of the alloy within a two-phase mixture is given by:

\[
G(x_B, T) = x_S G_S(x_B, T) + x_L G_L(x_B, T)
\]  

(17)
where \( x_S \) and \( x_L \) are the composition of the solid and liquid phase, respectively. The one-phase region is directly determined by the curve having the lowest Gibbs free energy while the two-phase region is simply determined by the equality between the Gibbs free energy of mixing in the liquid and solid states. For each temperature \( T \) between the melting points of the elements, the compositions that minimize the total GFE are determined. Therefore, at equilibrium, when the solid and liquid phases coexist \( (G_S = G_L) \), the solutions of Equation (16) form the solidus and liquidus curves in the binary phase diagram. The success of the theory has been confirmed in Figures 6 and 7 where the experimental data points perfectly match the theoretical predictions for the particular Au-Cu phase diagram. Furthermore, Figures 6 and 7 confirm the fact that there exist two types of size effects as mentioned in section 5. Indeed, the solid-liquid phase transition undergoes a stronger size effect \( (\xi/\xi_\infty = 1 - \alpha_{\text{shape}}/D) \) compared to a solid-solid phase transition \( (\xi/\xi_\infty = \sqrt{1 - \alpha_{\text{shape}}/D}) \). The reason is that a solid-liquid phase transition involves bond breaking, consequently involving electrons (fermions) while a solid-solid phase transition involves different vibrational characteristics between the two solid phases, consequently involving phonons (bosons). Therefore, Figures 6 and 7 illustrate the fermionic and bosonic nature of phase transitions.

Another effect that may play a significant role at the nanoscale is the stress within the nanoparticle. Indeed, the curvature of the nanoparticle increases as its size decreases; consequently, initiating higher strain and then higher stress within the nanoparticle. This effect becomes non-negligible for very small nanoparticles (~2-3 nm in size) i.e. clusters \([82–84]\). The large curvature of small nanoparticles is responsible of the strain which gives a volume contribution into the excess Gibbs energy of nanoparticles. Moreover, strain-stress effects are more important in binary and multi-elements compounds, because of the size mismatch between different atomic species, consequently affecting not only non-crystalline but also crystalline structures.

9. Conclusions

Nanothermodynamics is a theory developed by T.L. Hill in the early 1960s for small equilibrium systems and it has become one of the major formalisms for quantitative treatment of equilibrium nanoscale materials. The key concept in the theory is a difference between differential and integral forms of many non-extensive thermodynamic quantities due to the smallness of a system. Consequently, power laws naturally emerge as general features describing those complex nanoparticles due to their non-extensivity. Another important consequence of Hill’s theory is the sensitivity of nanoparticles to their
Figure 6. Top-view of the geometrical model representing (a) the rounded nanostar and (b) the pointed nanostar. a represents the length side of the decahedron. b, c, and t are the dimensions of the parallelepiped representing the branch of the nanostar (t being the thickness of the parallelepiped). d is the height of the trapeze connecting the decahedron to the parallelepiped. And h is the distance from the apex to the center of the nanostar. (c) Phase diagram of one Au$_{1-x}$Cu$_x$ rounded nanostar. The dimensions of the nanostar used for this calculation are a = 25 nm, b = 40 nm, c = 15 nm, d = 7 nm and t = 10 nm. (d) Phase diagram of one Au$_{1-x}$Cu$_x$ pointed nanostar. The dimensions of the nanostar used for this calculation are a = 50 nm and h = 10 nm. SEM images of the rounded and pointed nanostars at 200°C and 400°C. (e) Rounded nanostars at 200°C, (f) pointed nanostars at 200°C, (g) rounded nanostars at 400°C and (h) pointed nanostars at 400°C. The inset in (h) shows that the pointed nanostar still contains twins indicating that the pointed nanostar undergoes an atomic reorganization but not a melting transition. (Reproduced with the permission from Ref [120]).
Figure 7. Lower part of the Au-Cu phase diagram representing only the order–disorder phase transition at different composition range for cubic nanoparticles. (a) Order–disorder phase transition calculated for a cube having a side length equal to 15 nm. (b) TEM image showing a nanocube (size ~15 nm) heated at 120°C with its corresponding diffraction pattern. The red circles indicate the superlattice reflections’ characteristic of the ordered structure. (c) TEM image showing a nanocube (size ~15 nm) heated at 200°C with its corresponding diffraction pattern. (d) Order–disorder phase transition calculated for a cube having a side length equal to 15 nm. (e) TEM image showing a nanocube (size ~15 nm) heated at 200°C with its corresponding diffraction pattern confirming the fcc structure. (f) TEM image showing a nanocube (size ~15 nm) heated at 350°C with its corresponding diffraction pattern. The red circles indicate the superlattice reflections’ characteristic of the ordered structure. (g) Order–disorder phase transition calculated for a cube having a side length equal to 20 nm. (h) TEM image showing a nanocube (size ~20 nm) heated at 270°C with its corresponding diffraction pattern. The red circles indicate the superlattice reflections’ characteristic of the ordered structure. (i) TEM image showing a nanocube (size ~20 nm) heated at 350°C with its corresponding diffraction pattern. (Reproduced with the permission from Ref [92]).
environment. Therefore, by going from the macro-world to the nano-world, there is a transition from exponential laws describing a continuous material to power laws describing a discrete material. The appearance of those power laws is the result of strong correlations between the physico-chemical properties with the size, shape and environment of the nanoparticle. Finally, let’s remember Einstein’s quote about thermodynamics: ‘A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore, the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overturned’ [85].

**Acknowledgments**

The University of Arkansas at Little Rock is greatly acknowledged for financial support.

**Disclosure statement**

No potential conflict of interest was reported by the author.

**ORCID**

Grégory Guisbiers [http://orcid.org/0000-0002-4615-6014](http://orcid.org/0000-0002-4615-6014)

**References**

[1] Feynman RP. There’s plenty of room at the bottom. J Microelectromech Syst. 1992;1:60–66.
[2] Pennycook SJ, Varela M, Hetherington CJD, et al. Materials advances through aberration corrected electron microscopy. MRS Bull. 2006;31:36–43.
[3] Marks LD. What are the resolution limits in electron microscopes? Physics. 2013;6:82.
[4] Hawkes PW. Aberration correction past and present. Phil Trans R Soc A. 2009;367:3637–3664.
[5] Hill TL. Biographical Memoirs (2015) National Academy of Sciences, written by Ralph V. Chamberlin with a personal recollection by William A. Eaton. 1917-1924. [http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/hill-terrell.pdf](http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/hill-terrell.pdf)
[6] Hill TL. Thermodynamics of small systems. J Chem Phys. 1962;36:3182.
[7] Hill TL. Thermodynamics of small systems. Mineola, New York: Dover Publications; 1964.
[8] Hill TL. A different approach to nanothermodynamics. Nano Lett. 2001;1:273–275.
[9] Esfarjani K, Mansoori GA. Statistical mechanical modeling and its application to nanosystems. M.R.A.W. Schommers, editor. Handbook of Theoretical and Computational Nanotechnology; Stevenson Ranch, California: American Scientific Publishers. 2005.
[10] Leitner J, Sedmidubský D. Teaching nano-thermodynamics: Gibbs energy of single-component nanoparticles. World J Chem Educ. 2017;5:206–209.

[11] Kaptay G. The Gibbs equation versus the Kelvin and the Gibbs-Thomson equations to describe nucleation and equilibrium of nano-materials. J Nanosci Nanotechnol. 2011;12:1–9.

[12] Li ZH, Truhlar DG. Nanothermodynamics of metal nanoparticles. Chem Sci. 2014;5:2605–2624.

[13] Vakili-Nezhaad GR, Mansoori GA. An application of non-extensive statistical mechanics to nanosystems. J Comput Theor Nanosci. 2004;1:233–235.

[14] Chamberlin RV. The big world of nanothermodynamics. Entropy. 2015;17:52–73.

[15] Wang CX, Yang GW. Thermodynamics of metastable phase nucleation at the nanoscale. Mater Sci Eng R. 2005;49:157–202.

[16] Mansoori GA. Principles of nanotechnology. Singapore: World Scientific; 2005.

[17] Guenther G, Guillon O. Models of size-dependent nanoparticle melting tested on gold. J Mater Sci. 2014;49:7915–7932.

[18] Roduner E. Size matters: why nanomaterials are different. Chem Soc Rev. 2006;35:583–592.

[19] Prigogine I, Stuart AR. Evolution of size effects in chemical dynamics – part 2. United States of America: John Wiley & Sons; 1988.

[20] Tsallis C. Possible generalization of Boltzmann-Gibbs statistics. J Stat Mech. 1988;52:479–487.

[21] Tsallis C. The nonadditive entropy Sq and its applications in physics and elsewhere: some remarks. Entropy. 2011;13:1765–1804.

[22] Tsallis C. Thermodynamics and statistical mechanics for complex systems – foundations and applications. Acta Phys Pol B. 2015;46:1089–1101.

[23] Cartwright J. Roll over, Boltzmann. Physics World. 2014 May; 2014: 31–35.

[24] Penrose O. Foundations of statistical mechanics: a deductive treatment. Pergamon: Elsevier; 1970.

[25] Lucia U. A link between nano- and classical thermodynamics: dissipation analysis (The entropy generation approach in nano-thermodynamics). Entropy. 2015;17:1309–1328.

[26] García-Morales V, Cervera J, Pellicer J. Correct thermodynamic forces in Tsallis thermodynamics: connection with Hill nanothermodynamics. Phys Lett A. 2005;336:82–88.

[27] Feshbach H. Small systems – when does thermodynamics apply. Phys Today. 1987;40:9.

[28] Mohazzabi P, Mansoori GA. Why nanosystems and macroscopic systems behave differently? Int J Biomed Nanosci Nanotechnol. 2005;1:53–60.

[29] Murphy C, How can you calculate how many atoms are in a nanoparticle?, 2016, blog post, http://sustainable-nano.com/2016/07/28/how-many-atoms-are-in-a-nanoparticle/

[30] Wautelet M, Shirinyan AS. Thermodynamics: nano vs. macro. Pure Appl Chem. 2009;81:1921–1930.

[31] Hänggi P, Hilbert S, Dunkel J. Meaning of temperature in different thermostatistical ensembles. Phil Trans R Soc A. 2016;374:20150039.

[32] Vollath D, Fischer FD. Structural fluctuations in nanoparticles. J Nanopart Res. 2009;11:433–439.

[33] Kuzemsky AL. Thermodynamic limit in statistical physics. Int J Modern Phys B. 2009;28:1430004.

[34] Rajagopal AK, Pande CS, Abe S. Nanothermodynamics: a generic approach to material properties at nanoscale. arXiv preprint cond-mat/0403738. 2004.
[35] Cahill DG, Ford WK, Goodson KE, et al. Nanoscale thermal transport. J Appl Phys. 2003;93:793–818.
[36] Bourgeois O, Tainoff D, Tavakoli A, et al. Reduction of phonon mean free path: from low-temperature physics to room temperature applications in thermoelectricity. C R Phys. 2016;17:1154–1160.
[37] Wautelet M, Duvivier D. The characteristic dimensions of the nanoworld. Eur J Phys. 2007;28:953.
[38] Nano equation unveiled. Phys World. 2009;22:5. https://doi.org/10.1088/2058-7058/22/12/8.
[39] Guisbiers G. Size-dependent materials properties toward a universal equation. Nanoscale Res Lett. 2010;5:1132–1136.
[40] Guisbiers G, Buchaillot L. Universal size/shape-dependent law for characteristic temperatures. Phys Lett A. 2009;374:305–308.
[41] Guisbiers G, Jose-Yacaman M. Use of chemical functionalities to control stability of nanoparticles. Encyclopedia of Interfacial Chemistry: surface Science and Electrochemistry. 2017.
[42] Xiong S, Qi W, Cheng Y, et al. Universal relation for size dependent thermodynamic properties of metallic nanoparticles. Phys Chem Chem Phys. 2011;13:10652–10660.
[43] Yang CC, Xiao MX, Li W, et al. Size effects on Debye temperature, Einstein temperature, and volume thermal expansion coefficient of nanocrystals. Solid State Commun. 2006;139:148–152.
[44] Maioli P, Stoll T, Saucedo HE, et al. Mechanical vibrations of atomically defined metal clusters: from nano- to molecular-size oscillators. Nano Lett. 2018;18:6842–6849.
[45] Saucedo HE, Pelayo JJ, Salazar F, et al. Vibrational spectrum, low-temperature heat capacity, and Debye temperature of sodium clusters: the Na139 case. J Phys Chem C. 2013;117:11393–11398.
[46] Vanithakumari SC, Nanda KK. A universal relation for the cohesive energy of nanoparticles. Phys Lett A. 2008;372:6930–6934.
[47] Guisbiers G. Review on the analytical models describing melting at the nanoscale. J Nanosci Lett. 2012;2:8.
[48] Nanda KK. Size-dependent melting of nanoparticles: hundred years of thermodynamic model. Pramana. 2009;72:617–628.
[49] Calvo F. Thermodynamics of nanoalloys. Phys Chem Chem Phys. 2015;17:27922–27939.
[50] Guisbiers G, Buchaillot L. Modeling the melting enthalpy of nanomaterials. J Phys Chem C. 2009;113:3566–3568.
[51] Foster DM, Pavloudis T, Kioseoglou J, et al. Atomic-resolution imaging of surface and core melting in individual size-selected Au nanoclusters on carbon. Nat Commun. 2019;10:2583.
[52] Kjelstrup S, Schnell SK, Vlugt TJ, et al. Bridging scales with thermodynamics: from nano to macro. Adv Nat Sci. 2014;5:023002.
[53] Schnell SK, Liu X, Simon J-M, et al. Calculating thermodynamic properties from fluctuations at small scales. J Phys Chem A. 2011;115:10911–10918.
[54] Schnell SK, Vlugt TJH, Simon J-M, et al. Thermodynamics of small systems embedded in a reservoir: a detailed analysis of finite size effects. Mol Phys. 2012;110:1069–1079.
[55] Qi W. Nanoscopic thermodynamics. Acc Chem Res. 2016;49:1587–1595.
[56] Schnell SK, Vlugt TJH, Simon J-M, et al. Thermodynamics of a small system in a μT reservoir. Chem Phys Lett. 2011;504:199–201.
[57] Vanvechten JA, Wautelet M. Variation of semiconductor band-gaps with lattice temperature and with carrier temperature when these are not equal. Phys Rev B. 1981;23:5543–5550.
[58] Guisbiers G, Liu D, Jiang Q, et al. Theoretical predictions of wurtzite III-nitride nano-materials properties. Phys Chem Chem Phys. 2010;12:7203–7210.
[59] Bonham B, Guisbiers G. Thermal stability and optical properties of Si–Ge nanoparticles. Nanotechnology. 2017;28:245702.
[60] Guisbiers G, Wautelet M, Buchaillot L. Phase diagrams and optical properties of phosphide, arsenide, and antimonide binary and ternary III–V nanoalloys. Phys Rev B. 2009;79.
[61] Guisbiers G, Van Overschelde O, Wautelet M. Theoretical investigation of size and shape effects on the melting temperature and energy bandgap of TiO2 nanostructures. Appl Phys Lett. 2008;92.
[62] Li M, Li JC. Size effects on the band-gap of semiconductor compounds. Mater Lett. 2006;60:2526–2529.
[63] Zallen R. The physics of amorphous solids. United States of America: Wiley; 1983.
[64] Yang CC, Li S. Size, dimensionality, and constituent stoichiometry dependence of bandgap energies in semiconductor quantum dots and wires. J Phys Chem C. 2008;112:2851–2856.
[65] Yang CC, Mai YW. Thermodynamics at the nanoscale: a new approach to the investigation of unique physicochemical properties of nanomaterials. Mater Sci Eng R-Rep. 2014;79:1–40.
[66] Yang CC, Jiang Q. Size effect on the bandgap of II–VI semiconductor nanocrystals. Mater Sci Eng B. 2006;131:191–194.
[67] Geoffrion LD, Guisbiers G. Quantum confinement: size on the grill. Nanoscale (submitted). 2019.
[68] Marks LD, Peng L. Nanoparticle shape, thermodynamics and kinetics. J Phys-Condens Matter. 2016;28.
[69] Ringe E, Van Duyne RP, Marks LD. Wulff construction for alloy nanoparticles. Nano Lett. 2011;11:3399–3403.
[70] Jellinek J. Nanoalloys: tuning properties and characteristics through size and composition. Faraday Discuss. 2008;138:11–35.
[71] Ferrando R, Jellinek J, Johnston RL. Nanoalloys: from theory to applications of alloy clusters and nanoparticles. Chem Rev. 2008;108:845–910.
[72] Tanaka T, Hara S. Thermodynamic evaluation of nano-particle binary alloy phase diagrams. Zeitschrift Fur Metallkunde. 2001;92:1236–1241.
[73] Kaptay G. Nano-Calphad: extension of the Calphad method to systems with nano-phases and complexions. J Mater Sci. 2012;47:8320–8335.
[74] Liang LH, Liu D, Jiang Q. Size-dependent continuous binary solution phase diagram. Nanotechnology. 2003;14:438.
[75] Allen LH, Lai SL. MEMS-based scanning calorimeter for thermodynamic properties of nanostructures. Microscale Thermophys Eng. 1998;2:11–19.
[76] Lai SL, Carlsson JRA, Allen LH. Melting point depression of Al clusters generated during the early stages of film growth: nanocalorimetry measurements. Appl Phys Lett. 1998;72:1098–1100.
[77] Zhang M, Efremov MY, Schiettekatte F, et al. Size-dependent melting point depression of nanostructures: nanocalorimetric measurements. Phys Rev B. 2000;62:10548–10557.
[78] Barnard AS. Modelling of nanoparticles: approaches to morphology and evolution. Rep Prog Phys. 2010;73.
[79] Landman U. Materials by numbers: computations as tools of discovery. Proc Natl Acad Sci U S A. 2005;102:6671–6678.
[80] Guisbiers G, Mendoza-Perez R. Comment on ‘Phase stability and segregation behavior of nickel-based nanoalloys based on theory and simulation’. J Alloys Compd. 2017;723:1079–1081.

[81] Lee J, Park J, Tanaka T. Effects of interaction parameters and melting points of pure metals on the phase diagrams of the binary alloy nanoparticle systems: a classical approach based on the regular solution model. Calphad. 2009;33:377–381.

[82] Pirart J, Front A, Rapetti D, et al. Reversed size-dependent stabilization of ordered nanophases. Nat Commun. 2019;10:1982.

[83] Palomares-Baez JP, Panizon E, Ferrando R. Nanoscale effects on phase separation. Nano Lett. 2017;17:5394–5401.

[84] Ferrando R. Symmetry breaking and morphological instabilities in core-shell metallic nanoparticles. J Phys-Condens Matter. 2015;27.

[85] Einstein A. Autobiographical notes. Open Court; United States of America: Centennial edition; 1999.

[86] Hornyak GL, Tibbals HF, Dutta J, Moore JJ. Introduction to nanoscience & nanotechnology. Boca Raton, Florida: CRC Press; 2009.

[87] Guisbiers G, Mendoza-Cruz R, Bazán-Diaz L, et al. Electrum, the gold-silver alloy, from the bulk scale to the nanoscale: synthesis, properties, and segregation rules. ACS Nano. 2016;10:188–198.

[88] Park J, Lee J. Phase diagram reassessment of Ag–Au system including size effect. Calphad. 2008;32:135–141.

[89] Monji F, Jabbarieh MA. Thermodynamic model for prediction of binary alloy nanoparticle phase diagram including size dependent surface tension effect. Calphad. 2017;58:1–5.

[90] Zhao N, He YQ, Yang CC. A new approach to construct bulk and size-dependent continuous binary solution phase diagrams of alloys. RSC Adv. 2015;5:96323–96327.

[91] Guisbiers G, Mejia-Rosales S, Khanal S, et al. Gold copper nano-alloy, ‘Tumbaga’, in the era of nano: phase diagram and segregation. Nano Lett. 2014;14:6718–6726.

[92] Mendoza-Cruz R, Bazán-Diaz L, Velázquez-Salazar JJ, et al. Order-disorder phase transitions in Au–Cu nanocubes: from nano-thermodynamics to synthesis. Nanoscale. 2017;9:9267–9274.

[93] Hourlier D, Perrot P. Au-Si and Au-Ge phases diagrams for nanosystems. Mater Sci Forum. 2010;653:77–85.

[94] Tanaka T, Guisbiers G. Prediction of phase diagrams in nano-sized binary alloys. Mater Sci Forum. 2010;653:55–75.

[95] Sopousek J, Pinkas J, Brož P, et al. Ag-Cu colloid synthesis: bimetallic nanoparticle characterisation and thermal treatment. J Nanomater. 2014;638964.

[96] Atanasov I, Ferrando R, Johnston RL. Structure and solid solution properties of Cu–Ag nanoalloys. J Phys. 2014;26:275301.

[97] Zhao Z, Fischer A, Cheng D. Phase diagram and segregation of Ag–Co nanoalloys: insights from theory and simulation. Nanotechnology. 2016;27:115702.

[98] Kim DH, Kim HY, Ryu JH, et al. Phase diagram of Ag–Pd bimetallic nanoclusters by molecular dynamics simulations: solid-to-liquid transition and size-dependent behavior. Phys Chem Chem Phys. 2009;11:5079–5085.

[99] Sim K, Lee J. Phase stability of Ag–Sn alloy nanoparticles. J Alloys Compd. 2014;590:140–146.

[100] Lopes A, Tréglaia G, Mottet C, et al. Ordering and surface segregation in Co1–Cptc nanoparticles: a theoretical study from surface alloys to nanoalloys. Phys Rev B. 2015;91:035407.
Qi W, Li Y, Xiong S, et al. Modeling size and shape effects on the order–disorder phase-transition temperature of CoPt nanoparticles. Small. 2010;6:1996–1999.

Guisbiers G, Khanal S, Ruiz-Zepeda F, et al. Cu-Ni nano-alloy: mixed, core-shell or Janus nano-particle? Nanoscale. 2014;6:14630–14635.

Sopousek J, Vrestal J, Pinkas J, et al. Cu–Ni nanoalloy phase diagram – prediction and experiment. Calphad. 2014;45:33–39.

Shirinyan AS. Two-phase equilibrium states in individual Cu–Ni nanoparticles: size, depletion and hysteresis effects. Beilstein J Nanotechnol. 2015;6:1811–1820.

Jiang Q, Yang CC. Size effect on the phase stability of nanostructures. Curr Nanosci. 2008;4:179–200.

Guisbiers G, Mendoza-Pérez R, Bazán-Díaz L, et al. Size and shape effects on the phase diagrams of nickel-based bimetallic nanoalloys. J Phys Chem C. 2017;121:6930–6939.

Magnin Y, Zappelli A, Amara H, et al. Size dependent phase diagrams of nickel-carbon nanoparticles. Phys Rev Lett. 2015;115:205502.

Sopousek J, Vrestal J, Zemanova A, et al. Phase diagram prediction and particle characterization of Sn-Ag nano alloy for low melting point lead-free solders. J Min Metall Sect B Metall. 2012;48:419–425.

Ghasemi M, Zanolli Z, Stankovski M, et al. Size- and shape-dependent phase diagram of In–Sb nano-alloys. Nanoscale. 2015;7:17387–17396.

Mendoza-Perez R, Guisbiers G. Bimetallic Pt- Pd nano-catalyst: size, shape and composition matter. Nanotechnology. 2019;30(30):305702.

Guisbiers G, Abudukelimu G, Hourlier D. Size-dependent catalytic and melting properties of platinum-palladium nanoparticles. Nanoscale Res Lett. 2011;6:396.

Pohl J, Stahl C, Albe K. Size-dependent phase diagrams of metallic alloys: a Monte Carlo simulation study on order–disorder transitions in Pt–Rh nanoparticles. Beilstein J Nanotechnol. 2012;3:1–11.

Dahan Y, Makov G, Shneck RZ. Nanometric size dependent phase diagram of Bi–Sn. Calphad. 2016;53:136–145.

Guisbiers G, Kazan M, Van Overschelde O, et al. Mechanical and thermal properties of metallic and semiconductive nanostructures. J Phys Chem C. 2008;112:4097–4103.

Guisbiers G, Lara HH, Mendoza-Cruz R, et al. Inhibition of Candida albicans biofilm by pure selenium nanoparticles synthesized by pulsed laser ablation in liquids. Nanomed. 2017;13:1095–1103.

Vossmeyer T, Katsikas L, Giersig M, et al. Cds nanoclusters – synthesis, characterization, size-dependent oscillator strength, temperature shift of the excitonic-transition energy, and reversible absorbency shift. J Phys Chem. 1994;98:7665–7673.

Torimoto T, Kontani H, Shibutani Y, et al. Characterization of ultrasmall CdS nanoparticles prepared by the size-selective photoetching technique. J Phys Chem B. 2001;105:6838–6845.

Soltani N, Gharibshahi E, Saion E. Band gap of cubic and hexagonal Cds quantum dots – experimental and theoretical studies. Chalcogenide Lett. 2012;9:321–328.

Banerjee R, Jayakrishnan R, Ayyub P. Effect of the size-induced structural transformation on the band gap in CdS nanoparticles. J Phys-Condens Matter. 2000;12:10647–10654.

Bazán-Díaz L, Mendoza-Cruz R, Velázquez-Salazar JJ, et al. Gold–copper nanostars as photo-thermal agents: synthesis and advanced electron microscopy characterization. Nanoscale. 2015;7:20734–20742.