PHYSICAL REVIEW B **76**, 045428 (2007)

Melting point depression of nanosolids: Nonextensive thermodynamics approach

Pierre Letellier, Alain Mayaffre, and Mireille Turmine*
Université Pierre et Marie Curie, Paris, France;
Ecole Nationale Supérieure de Chimie Paris (ENSCP), CNRS, UMR 7575, Paris F-75005, France;
and Energétique et Réactivité aux Interfaces, UPMC, case 39, 4 place Jussieu, 75252 Paris Cedex 05, France

(Received 22 February 2007; revised manuscript received 18 May 2007; published 27 July 2007)

The concepts of nonextensive thermodynamics introduced in previous work can be used to show that depression or elevation of melting points for a nanosolid (nanoparticles, nanowires, films, and embedded particles) depends on the nanoparticle size according to power laws whose significance can be specified. The Gibbs-Thompson relation seems to be a particular case of these relations. This approach is based on a thermodynamic description involving the introduction of an extensity χ into the internal energy expression. χ is an Euler function of the particle mass with a homogeneity degree m, which can be other than 1; m is the thermodynamic dimension of the system. Here, we show how various behaviors of nanosolids published in the literature can be analyzed according to this theory.

DOI: 10.1103/PhysRevB.76.045428 PACS number(s): 65.80.+n, 05.70.−a, 64.70.Dv, 82.60.Qr

I. INTRODUCTION

The phenomenon of melting point depression for nanosolids was first described at the beginning of the 20th century[1] and has been formalized, for a spherical particle of radius r, by the relation known as that of Gibbs-Thompson. This links the difference between the melting point of the particle T_x and the melting point of the material T_m, in its form of unlimited phase[2] (no size effect), by

$$T_m - T_x = \Delta T = \frac{T_m V_{(T_x)}}{\Delta H_m}\frac{2\gamma^{\mathrm{SL}}}{r}. \tag{1}$$

At temperature T_x, $V_{(T_x)}$ is the molar volume of the solid, γ^{SL} is the surface tension between the solid and the liquid, and ΔH_m is the melting molar enthalpy of the solid ($\Delta H_m > 0$, endothermic). This relation is copied from that of Kelvin, established to describe liquid-vapor equilibrium for liquid drops. It has been thoroughly discussed by Defay and Prigogine in Ref. 3. The application of the Gibbs-Thompson relation is not entirely straightforward because real particles of nanosolid are not, in general, perfect spheres. This is the case, for example, of mineral or organic crystals and their assemblies, of polymer aggregates, and of films. For some materials, like microporous materials, it is difficult to describe their spatial structure from the classical geometrical variables of dimension (volume, surface, and length) and some authors[4–7] have suggested using fractal approaches. In such conditions, the concept of liquid-solid interfacial tension γ^{SL} cannot apply. However, the phenomenon of melting depression and elevation is an experimental reality observed for numerous nanosolids of different sizes and forms.[8–17] Christenson[18] reviewed experimental work involving freezing and melting in confinement and also considered the behavior of porous systems. Numerous authors have tried to formalize this phenomenon from the relations of classical thermodynamics,[19] or by using molecular approaches.[20–25] Most of these studies involve the precondition that ΔT increases or decreases with decreasing particle size.

As a consequence, it would be interesting to tackle this issue by applying relations of nonextensive thermodynamics (NET) introduced in 2004.[26] The basis is identical to that of classical thermodynamics, with the same functions of state, but supposes that these functions of state can be nonextensive. This property is introduced by means of integer or fractional thermodynamic dimensions. As a result, various physicochemical behaviors can be described by power laws without having recourse to the concept of fractality. This approach is particularly adapted to the description of complex systems (including porous systems, interpenetrated phases, dispersed solutions, nanoparticles, and films). To explain our approach, we will first describe some of the bases of NET.[26]

II. THEORY

A. Conceptual bases of nonextensive thermodynamics

The description of the behavior of a system defined by its content (n_1, n_2, n_i moles) requires the usual variables S, V, and n_i, and a variable of extensity χ. The internal energy can then be written as

$$dU = TdS - PdV + \sum \mu_i dn_i + \tau d\chi, \tag{2}$$

Where τ is an intensive tension extent associated with χ. This relation is classical[27] and in the case of interfacial systems, χ is associated with an area and τ with a surface tension. Classically, in thermodynamics, the variables of extensity associated with tension extents are assumed to be extensive variables, i.e., Euler's functions of the system mass of order $m=1$.[28] We considered the possibility that they are not extensive ($m \neq 1$) and consequently that the properties of χ have to specified. In a system consisting of n_1 moles of 1, n_2 moles of 2, and n_i moles of i, the extensity χ is a function of the system mass

$$\chi = \chi(n_1, n_2, \ldots, n_i). \tag{3}$$

By convention, this extent has the property of Euler's function of order m. If the system content is multiplied by λ, then

$$\chi_\lambda = \chi(\lambda n_1, \lambda n_2, \ldots, \lambda n_i) = \lambda^m \chi. \tag{4}$$

The parameter m is the degree of homogeneity of the Euler function, named by convention, the thermodynamic dimension of the system. Its value can be equal to 1, in which case classical thermodynamics applies. The introduction of nonextensive thermodynamics in the extensity magnitudes implies that the functions of state of thermodynamics (U, S, etc.) are not extensive. Consequently, the tension extents associated with the extensities may not be intensive. We chose, by convention, to conserve this property for the temperature T (Ref. 29) and for τ. For consistency, the chemical potentials and the pressures become nonintensive extents; this means that they vary with the system mass. For a nonextensive system constituted of n moles of compound, of volume V, of extensity χ, and of dimension m, there is a relationship between the pressure of the nonextensive system ${}^{\mathrm{NE}}P$ and the pressure of the environment P,

$$({}^{\mathrm{NE}}P - P) = \tau\frac{d\chi}{dV} = m\frac{\tau\chi}{V}. \tag{5}$$

This relation generalizes Laplace's relationship for nonextensive systems. It does not involve a radius of curvature or precise geometrical borders of the nonextensive system but is defined only from physicochemical parameters. This obviously allows the solution to be found if the geometry is simple. In the case of liquid drop of interfacial tension γ^{LV} and radius r, the pressure difference between the inside of the drop (${}^{\mathrm{NE}}P = P_d$) and the external pressure of the gaseous atmosphere is obtained by introducing the interfacial parameters into Eq. (5), $\tau = \gamma^{\mathrm{LV}}$, $\chi = A^{\mathrm{LV}}$. Note that when the drop volume is multiplied by λ, the area A^{LV} is multiplied by $\lambda^{2/3}$. The area is then an extensity of dimension $m = 2/3$ toward the mass or the drop volume. The liquid drop is a *nonextensive phase* with a thermodynamic dimension equal to 2/3. We can write

$$(P_d - P) = m\frac{\tau\chi}{V} = \frac{2}{3}\frac{\gamma^{\mathrm{LV}}A^{\mathrm{LV}}}{V} = 2\frac{\gamma^{\mathrm{LV}}}{r}, \tag{6}$$

which corresponds to Laplace's relationship.

We will apply these NET definition relations to the change of melting point of a nanosolid, when the size and the shape are modified. We will suppose that the solid constitutes a nonextensive phase (Fig. 1).

B. Melting point

The equilibrium between the nanosolid in the form of nonextensive phase and the liquid at the melting point T_x is expressed by writing the equality of the chemical potentials of the compound under its two forms. The solid (S) is at the pressure ${}^{\mathrm{NE}}P$ of the nonextensive phase; the liquid (liq) is subject to the external pressure P,

$$\mu^S_{(T_x,{}^{\mathrm{NE}}P)} = \mu^{\mathrm{liq}}_{(T_x,P)}. \tag{7}$$

At temperature T_x and constant content, the chemical potential of pure solid varies with the pressure P according to the relation

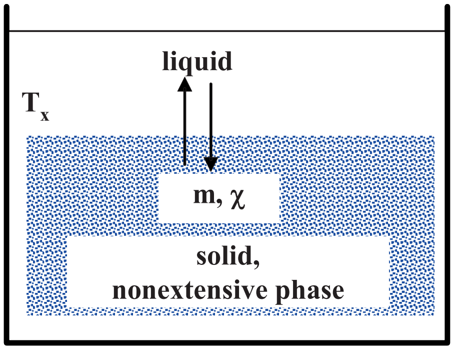

FIG. 1. (Color online) Scheme of the considered system. The nanosolid constitutes a nonextensive phase of dimension m and of extensity χ. This solid is in contact with the liquid phase at temperature T_x.

$$\left[\frac{\partial \mu^S_{(T_x)}}{\partial P}\right]_{T_x,n} = V_{(T_x)}, \tag{8}$$

Where $V_{(T_x)}$ is the molar volume of pure solid at temperature T_x. If its value varies slightly with the pressure, the integration of Eq. (8) gives

$$\mu^S_{(T_x,{}^{\mathrm{NE}}P)} = \mu^S_{(T_x,P)} + V_{(T_x)}({}^{\mathrm{NE}}P - P). \tag{9}$$

By considering the volume V which corresponds to the volume occupied by the nanosolid in the system, then

$$\mu^S_{(T_x,{}^{\mathrm{NE}}P)} = \mu^S_{(T_x,P)} + V_{(T_x)}m\tau\frac{\chi}{V}. \tag{10}$$

At the pressure P of the environment, the equilibrium condition [Eq. (7)] can be written as

$$\mu^{\mathrm{liq}}_{(T_x)} = \mu^S_{(T_x)} + V_{(T_x)}m\tau\frac{\chi}{V}. \tag{11}$$

The pressure being constant (isobar condition), we removed P from the notation of the chemical potential for clarity. The free energy of melting at temperature T_x, $\Delta G_{m(T_x)}$, is linked to the characteristic parameters of the nonextensive phase

$$\mu^{\mathrm{liq}}_{(T_x)} - \mu^S_{(T_x)} = \Delta G_{m(T_x)} = V_{(T_x)}m\tau\frac{\chi}{V}. \tag{12}$$

At the melting temperature of the solid in the form of an unlimited phase (T_m), the melting free energy is null. The integration of the Gibbs-Helmholtz relation between T_m and T_x leads to

$$\frac{\Delta G_{m(T_x)}}{T_x} = -\int_{T_m}^{T_x} \Delta H_m \frac{dT}{T^2}, \tag{13}$$

where ΔH_m is the melting molar enthalpy of pure solid at ambient pressure P. As the melting enthalpy varies slightly in the temperature range considered for integration, one can write

$$\Delta G_{m(T_x)} = \Delta H_m\left(1 - \frac{T_x}{T_m}\right) = V_{(T_x)} m \tau \frac{\chi}{V}. \tag{14}$$

Then, the melting temperature T_x of the nonextensive phase can be easily linked to the melting point T_m of the unlimited phase by the following equation which can be written in two different ways:

$$T_m - T_x = \Delta T = T_m \frac{V_{(T_x)} m \tau \frac{\chi}{V}}{\Delta H_m} = T_m \frac{M^\circ m \tau \frac{\chi}{M}}{\Delta H_m}, \tag{15}$$

where M° is the molecular weight and M the mass of the solid.

III. APPLICATION TO THE MELTING TEMPERATURE OF A NONEXTENSIVE PHASE

Consider first the case where the geometry of the nonextensive phase is sufficiently well defined for the extensity χ to be identified with an area.

A. Extensity is an area

1. Gibbs-Thompson law

Consider a solid particle of spherical shape of radius r in equilibrium with a molten liquid. In this case, dimension m is equal to $2/3$. If the extensity is identified with the solid-liquid area A^{SL}, the tension τ with the surface tension γ^{SL}, and the volume of the nonextensive phase to that of the particle, the Gibbs-Thompson relation is then found to be

$$\Delta T = \frac{T_m V_{i(T_x)}}{\Delta H_m}\left(\frac{2}{3}\gamma^{SL}\frac{4\pi r^2}{\frac{4}{3}\pi r^3}\right) = \frac{T_m V_{(T_x)}}{\Delta H_m}\frac{2\gamma^{SL}}{r}. \tag{16}$$

Note that this relation supposes that the solid-liquid surface tension γ^{SL} is experimentally accessible, because the melting temperature variations of a material in spherical particles of known sizes can be accurately determined. The same is true for the Ostwald-Freundlich expression which governs nanoparticle solubility.[30,31] It is thus surprisingly simple to determine an extent which is generally calculated by semiempirical approaches and wettability studies.[32–34] However, in addition to the experimental difficulties of determining the particle size (and the particles must be spherical), the introduction of a solid-liquid interfacial tension supposes that the interface is at equilibrium and of constant curvature: this can only be an assumption in the case of a solid. The result is that the validity of the determination of γ^{SL} by this method is uncertain.

In our approach, this problem does not explicitly appear because Eq. (15) is based on a property of the system's response to the variations of its mass (extensity); neither the interfacial area nor the use of Laplace's relation is required. Thus, it seems appropriate to express the previous equilibrium without identifying the tension τ as the interfacial tension γ^{SL} in the Gibbs-Thompson law and to write the depression melting point in the form

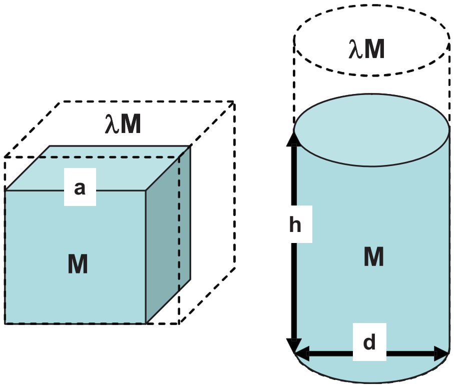

FIG. 2. (Color online) Two kinds of geometrically defined particles are considered. Their mass is multiplied by λ. The cube increases in size with no change in shape. The cylinder increases in size with no change in base area.

$$\Delta T = \frac{T_m V_{(T_x)}}{\Delta H_m}\frac{2\tau}{r}. \tag{17}$$

We will proceed on this basis for the following cases.

2. Particle is not spherical

Equation (15) can be used to address the case of particles of diverse forms and especially those corresponding to classical unit cells, for example, a cube of edge a and of volume a^3. Initially, the thermodynamic dimension of the system m is determined by multiplying its mass by a number λ and leaving its form unchanged. In this operation, the volume will also be multiplied by λ (at constant density), whereas the surface area of the cube, $6a^2$, will be multiplied by $\lambda^{2/3}$. The thermodynamic dimension of the system is $m=2/3$. Then,

$$\Delta T = T_m \frac{V_{(T_x)}\frac{2}{3}\tau\frac{6a^2}{a^3}}{\Delta H_m} = \frac{T_m V_{(T_x)}}{\Delta H_m}\frac{4\tau}{a}. \tag{18}$$

The melting point depression of a cubic nanosolid is related to the length of the cube edge. The depression is greater as the edge length decreases.

Our approach has its limitations because the extensities of some structures do not always display the properties of Euler's functions. Consider, for example, a cylindrical particle of height h whose base is of diameter d (Fig. 2). Suppose that the particle grows without any change in base area but with increasing height h. The cylinder volume is $V=(\pi d^2/4)h$ and the area $A=2(\pi d^2/4)+\pi dh$. If the cylinder mass is multiplied by λ, only h will be multiplied by λ, and consequently the surface area of cylinder will become $A_\lambda=2(\pi d^2/4)+\lambda\pi dh$. In this case, the area is not an Euler function of the mass and the relations of NET do not apply. For this reason, it must be systematically verified that the extensity is an Euler function of the mass before Eq. (15) can be applied. However, for cylindrical particles that are sufficiently long for the surface area of the base to be negligible relative to the surface area of the sides ($h \gg d/2$), the total surface area approximates to an Euler function of order 1 of the mass: the dimension of the system is 1. Then,

$$\Delta T = T_m \frac{V_{(T_x)} \tau \frac{4\pi dh}{\pi d^2 h}}{\Delta H_m} = \frac{T_m V_{(T_x)}}{\Delta H_m} \frac{4\tau}{d}. \tag{19}$$

In this case, the melting point depression of particles is dependent on the cylinder diameter but is independent of its length.

There are many examples which can be used to illustrate the value of applying Eq. (15) to objects of various sizes and forms. We will consider the case of real nanoparticles whose spatial structure cannot be described simply from classical dimensions (volumes, areas, and lengths).

B. General case. Power laws: Consequence of the NET

Consider a given mass M of solid presumed to constitute a nonextensive phase. The extensity χ is a homogeneous function of order m of the system mass, so the ratio between χ and M is a homogeneous function of order $(m-1)$ of the solid mass. This corresponds to

$$\frac{\chi}{M} = kM^{m-1}, \tag{20}$$

where k is a characteristic constant of the nonextensive phase considered. This condition combined with Eq. (15) leads to

$$\Delta T = T_m \frac{M^\circ m\tau k}{\Delta H_m} M^{m-1}. \tag{21}$$

This can be written in logarithmic form

$$\ln(\Delta T) = \ln\left(T_m \frac{M^\circ mY}{\Delta H_m}\right) + (m-1)\ln M. \tag{22}$$

To simplify the notation, the product τk is replaced by Y. Y is a characteristic extent of the solid. Its unit u depends on the value of m, $u = \mathrm{J\ kg}^{-m}$. Thus, we show that the melting point depression or elevation of a nanosolid *follows* a power law of the particle mass.

For the melting point of the nanosolid T_x to find its value T_m when the solid mass becomes large (unlimited phase), it is necessary that $m < 1$. Equation (21) implies that for positive m and τ, the melting point of the nanosolid must be depressed as the particle size decreases: this is the classical behavior. However, the theory does not require this behavior. Indeed, situations in which m or τ (Y) are negative can be envisaged, leading to the opposite phenomenon, i.e., an increase in the melting point as particle size decreases. Behavior of this type has been observed, mostly for particles embedded in a matrix[35–37] and for Vycor glass as reported by Christenson.[18]

1. Case of nanoparticles of dimension m and of mass M_p

Above, we considered a mass of solid without specifying its state of division. We will now examine the behavior of a solid in the form of identical nanoparticles, having the same property of nonextensive phase of dimension m. The mass of a particle is M_p, its volume V_p and its extensity χ_p. We will assume that any addition of solid to the system will only increase the number N of nanoparticles. This situation is described by the following relations:

$$M = NM_p,$$

$$\chi = N\chi_p,$$

$$\frac{\chi}{V} = \frac{\chi_p}{V_p} = kM_p^{m-1}, \tag{23}$$

and then,

$$\ln(\Delta T) = \ln\left(T_m \frac{M^\circ mY}{\Delta H_m}\right) + (m-1)\ln M_p. \tag{24}$$

The depression or elevation of melting point then depends on the *nanoparticle mass* according to a power law.

2. Applications to real systems

The validity of the previous relations is difficult to judge because the data in the literature concerning melting point depression are generally given according to the "particle size." Size may be described by a radius for presumed spherical particles, a diameter for nanowires, or a thickness for films. We thus modified the form of the previous equations so as to make them more generally applicable and take into account all measurements reported in the literature without considering particular forms for the nanosolids.

Our reasoning is as follows. Suppose that the nanosolid size is characterized by a dimension (radius, diameter, and thickness) which is noted ω. We will suppose that the extensity χ and the volume are Euler's functions of ω so

$$V = V_{(\omega)} = \alpha\omega^q,$$

$$\chi = \chi_{(\omega)} = \beta\omega^p. \tag{25}$$

The pressure difference between the nonextensive solid phase and the solution is then written as

$${}^{\mathrm{NE}}P - P = \tau\frac{d\chi}{dV} = \tau\frac{\beta p}{\alpha q}\omega^{p-q}. \tag{26}$$

Similar reasoning leads to the melting temperature variation with the size ω of the particles according to a power law

$$T_m - T_x = \Delta T = T_m \frac{V_{(T_x)}\frac{\beta}{\alpha}\tau}{\Delta H_m}\frac{p}{q}\omega^{p-q} = T_m \frac{M^\circ Y_\omega}{\Delta H_m}\frac{p}{q}\omega^{\eta}. \tag{27}$$

By convention, we will note $p\text{-}q = \eta$ and $Y_\omega = (V_{(T_x)}/M^\circ) \times (\beta/\alpha)\tau$.

The form of the Gibbs-Thompson relation can be verified by taking the radius as dimension $\omega = r$, $p = 2$, and $q = 3$. In this case, for a compound of density ρ, $Y_\omega = 3\gamma^{\mathrm{SL}}/\rho(\mathrm{J\ m\ kg}^{-1})$.

We will now test the validity of Eq. (27) under its logarithmic form for published data.

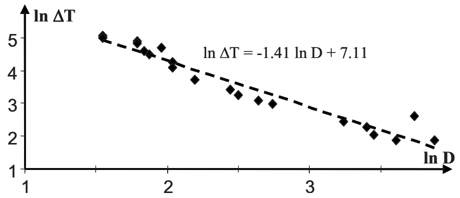

FIG. 3. Plot of ln(ΔT) against ln(D) for Pb particles according to the data in Ref. 39 The diameter D is expressed in nanometers.

$$\ln(\Delta T) = \ln\left(T_m \frac{M^{\circ} Y_{\omega} p}{\Delta H_m q}\right) + \eta \ln(\omega). \tag{28}$$

The plot of ln(ΔT) against the logarithm of the dimension ω, chosen by the author of the study to characterize nanosolid size, will only be a straight line if the extensities and the masses are Euler's functions of dimension and if variations of the parameters Y_{ω}, p, and q with the temperature are small.

IV. ANALYSES OF PUBLISHED DATA

A. Nanoparticles

First, consider the case where the nanosolid is in the form of nanoparticles. We will examine two series of data. In example 1, we examined the results reported by Ben David *et al.*[38] and cited by Qi[39] concerning ultrafine Pb particles. Figure 3 shows ln(ΔT) plotted against the logarithm of the particle diameter (in nanometers).

The line of correlation is excellent, with a y-axis intercept of 7.11 and $\eta = -1.41$ which is higher (in absolute value) than that corresponding to the Gibbs-Thompson relation ($\eta = -1$). The value of η takes into account both the nonextensivity of the mass and the extensity with respect to the measured dimension. This value indicates that if the mass varies with ω (with $q=3$) as is generally the case, then the extensity χ of the nanoparticles would be of power $p=1.59$ with respect to the nanoparticle diameter. This value is lower than 2 which would be characteristic of an area. The result is that the extensity χ increases less quickly with ω than an area would.

In example 2, we examined the work of Lai *et al.*[40] on tin nanoparticles. These particles are formed by thermal evaporation. For the small amounts of Sn deposited, the films are discontinuous and form self-assembled nanometer-sized islands on the inert substrate. According to the authors, in contrast to embedding metal particles in bulk matrix, this type of sample preparation produces spherical Sn particles with high purity and free surfaces; this system is thus ideal for studies of melting of small metal particles. We plotted the experimental ln(ΔT) against the logarithm of the particle radius (in nanometers) in Fig. 4.

Once again, an excellent linear correlation is found; the y-axis intercept is 5.995 and the slope is $\eta = -1.20$, lower than -1 which corresponds to spherical particles. As for the previous case, the extensity χ increases less quickly than the area with the particle radius: $p=1.8$.

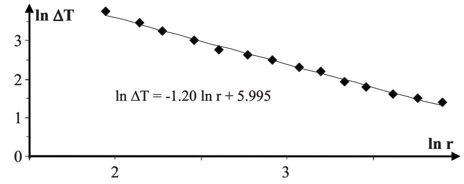

FIG. 4. Plot of ln(ΔT) against ln(r) for tin particles, from Ref. 40 ΔT is the melting point depression in °C and r is the particle radius in nanometers.

B. Nanowires

Metal nanowires have attracted a great deal of research interest in recent years because of their importance in fundamental low-dimensional physics research as well as for technological applications. The melting behavior of Zn nanowires with various diameters embedded in the holes of a porous anodic alumina membrane has been studied by Wang *et al.*[41] These nanosolids are particularly interesting because they are assumed to be composed of one-dimensional nanostructures. Differential scanning calorimetry showed that the melting temperature of the Zn nanowire arrays was strongly dependent on nanowire size. We report the values of the logarithm of melting point depression against the logarithm of nanowire diameter (in nanometers) in Fig. 5.

An excellent linear correlation is obtained with a y-axis intercept of 4.27 and a slope $\eta = -0.57$. This behavior is very different from that observed for nanoparticles; indeed, if one supposes that $q=3$ as above, then p is equal to 2.43. In this case, the extensity increases more quickly than the particle area and obviously does not follow the Gibbs-Thompson law, contrary to the expectations of the authors.

C. Films

Films of nanometric thickness can be considered alongside of nanoparticles: the dimension ω is in this case the film thickness. Two series of data extracted from the literature will be analyzed.

In example 1, Olson *et al.*[42] described bismuth films. The particles were formed by evaporating bismuth onto a silicon nitride substrate, which was then heated. The particles self-assemble into truncated spherical particles. At mean film thicknesses below 5 nm, mean particle sizes increased linearly with deposition thickness but for 10 nm thick films, particle size increased rapidly. A plot of the logarithms of melting point depressions against film thickness is given in Fig. 6.

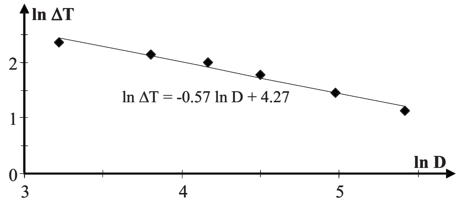

FIG. 5. Plot of ln(ΔT) against ln(D) for zinc nanowires in an alumina matrix from data extracted from Ref. 41 ΔT is the melting point depression in °C and D is the particle diameter in nanometers.

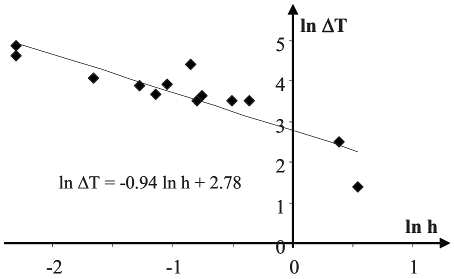

FIG. 6. ln(ΔT) plotted against ln(h) for bismuth films. h is the thickness of the film in nanometers. Data extracted from Ref. 42.

A reasonable linear correlation is obtained. The y-axis intercept is 2.78 and the slope is $\eta = -0.94$, which as for nanowires is greater than -1. Supposing that $q = 3$, the extensity varies more than the area with the increase of the nanoparticle film thickness ($p = 2.06$).

In example 2, the melting point depression phenomenon can also be considered for organic nanosolids. Unruh *et al.*[43] described the behavior of films of triglyceride nanoparticles (Fig. 7).

The linear correlation is satisfactory. The y-axis intercept is 4.16 and the slope is $\eta = -0.71$; this is greater than -1 as was the case for mineral films. Supposing that $q = 3$, the extensity varies more than the area with the increase of the nanoparticle film thickness ($p = 2.29$).

The description of the behavior of films is worse than those for the previous examples. This is probably because films consist of nanosolids in juxtaposition.

D. Melting point elevation

The equations that we have developed can also be used to consider melting point elevation. This situation is mainly found for particles that are coated or embedded in a matrix.[36,37,44–47] There are many explanations proposed for this phenomenon. All these explanations use the interfacial energy between the liquid compound and the solid constituting the matrix. It is certain that for embedded particles, the borders between the particle and its environment are very badly defined geometrically; we show, below, that our approach can be used to overcome this problem. We analyzed the values published by Lu and Jin[37] concerning the variations of melting point with the particle size for nanoparticles of In embedded in an Al matrix. Two kinds of In/Al nanogranular samples were prepared by means of melt spinning and ball milling. For melt-spun nanoparticles, the melting point increased as the particle size decreased, whereas for ball-milled nanoparticles, the melting point decreases with particle size. We exploited these two data series. For the melting point elevation series, we changed the sign in relation (28) such that extents were positive under the logarithmic terms

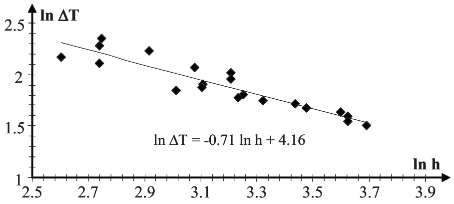

FIG. 7. Plot of ln(ΔT) against ln(h) for films of triglycerides. h is the thickness of the film in nanometers. Data extracted from Ref. 43.

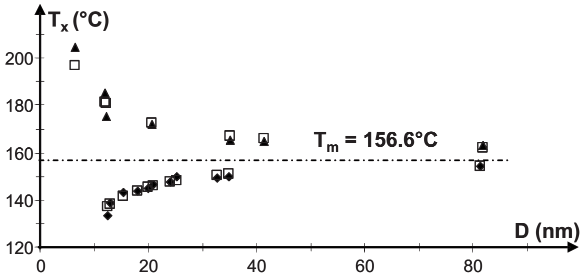

FIG. 8. Experimental (black points) and calculated (open squares) values of melting point T_x against the particle size (diameter D) for In nanoparticles embedded in an Al matrix prepared by melt spinning (triangles) and ball milling (diamonds) (Ref. 37).

$$\ln(T_m - T_x) = \ln\left(T_m \frac{M^\circ Y_\omega p}{\Delta H_m\, q}\right) + \eta \ln(\omega). \qquad (28')$$

The ln/ln correlations are excellent for both melting point elevation and depression data series. We plotted the experimental data and the calculated values (Fig. 8) with the following parameters.

(a) For melting point elevation, $\eta = -0.805$ and the y-axis intercept is 5.203.

(b) For melting point depression, $\eta = -1.149$ and the y-axis intercept is 5.858.

For the melting point depression, if we take $q = 3$ for the volume dimension, then $p = 1.851$. Thus, the extensity varies less quickly than the area with the particle mass. In the case of the melting point elevation, the value of τ is *negative*. p is equal to 2.195, taking, by convention, $q = 3$. Thus, the extensity varies more quickly than the area with the particle mass. This approach allows description of the particle and its matrix. According to the matrix structure or the particle shape, one of these two behaviors is observed; the sign of τ expresses and formalizes this difference of behavior. Thus, under constraint, the sign of τ can be reversed.

Remark. To analyze the behaviors of embedded particles, we considered only one extensity χ. This seems sufficient in the case examined to provide a good representation of the experimental results. However, since the growth of a system in contact with a support or a matrix is considered, other dimensions can intervene. This is illustrated by Auer and Frenkel in a recent article[48] in which they show the importance of the line tension in the phenomenon of aggregation. This raises the issue of the form of the relations we propose in such a situation. In fact, these relations can easily be generalized and use several extensities. Equation (5) becomes

$$^{\mathrm{NE}}P - P = \sum_i \tau_i \frac{d\chi_i}{dV} = \sum_i m_i \tau_i \frac{\chi_i}{V}. \qquad (29)$$

When one of these extensities is a triple line, then

$$^{\mathrm{NE}}P - P = \sum_{i-1} m_i \tau_i \frac{\chi_i}{V} + m_{\mathrm{line}} \frac{\tau_{\mathrm{line}} \chi_{\mathrm{line}}}{V}. \quad (30)$$

In this case, the dimension m_{line} is then equal to $1/3$, τ_{line} is the line tension, and χ_{line} is the length of the considered line. The exploitation of this relation is possible only if the particle shape is known and if its interfaces with the matrix can be characterized geometrically. An application of this will be found in a paper concerning contact angles,[49] in which we show that for nanodrops, the term for line tension can become dominant in Eq. (30).

V. CONCLUSION

We analyzed data published in the literature and showed that for all the experimental models considered, the melting point depression of nanosolids *follows* a power law with respect to their dimension, as do nanoparticles, nanowires, and films. The NET relations provide a theoretical justification for these behaviors and give a meaning to the various parameters implied in these laws. Note, however, that our developments have their limitations.

The first and undoubtedly most important is that the developments that we propose address only small particles, without nuclearity being too weak (i.e., made of few atoms or molecules). Many authors suppose that for these systems, there is a new state of matter, intermediate between the atom and the crystal.[50,51] Kubo, in 1962,[52] thus suggests that an isolated atom, or a few atoms linked together in a cluster, for example, in a molecule, should be considered to possess discrete electron levels, introducing a *quantum-size effect*. It has been shown, indeed, that the thermodynamic properties of a metallic cluster vary with the number of atoms n which it contains in solutions[53,54] or in the vapor phase.[55,56]

Concerning melting points, the calorimetric measurements reported by Jarrold and co-workers[57,58] indicate that small clusters of tin and gallium—in the size range of 17–55 atoms—have *higher than bulk* melting temperatures (T_m bulk). A striking experimental result from the same group showed extreme size sensitivity in the nature of the heat capacity of Ga clusters of 30–55 atoms.[59] Recently, Joshi *et al.*[60] presented a study of extensive *ab initio* molecular dynamic simulations with Ga_{30} and Ga_{31}, where they attribute the origin of this size sensitivity of heat capacities to the relative order in their respective ground state geometries. It turns out that the addition of even one atom changes the heat capacity dramatically.

The relations that we propose make sense if the aggregates have sufficient nuclearity for average behaviors to appear, and this which supposes several hundreds of atoms, and sizes higher than 1 nm (a spherical aggregate of silver of 2 nm comprises approximately 2000 atoms). This condition of size is not the only one which limits the application of the relations we suggest. They can apply only if

(a) the system is at equilibrium,

(b) the extensities are Euler's functions of the dimension, and

(c) the variation of parameters p, q, Y_ω, or their association is largely independent of the temperature. This property cannot be taken as a general condition.

Our analysis shows that for systems of a nanometric magnitude, the laws of thermodynamics must be reconsidered.[61,62] This led us to consider a thermodynamic approach based on nonextensive functions of state, but there are undoubtedly other possible approaches. However, our approach allows simple and suitable description of the physicochemical behaviors of many complex systems, including those extracted from the literature and presented in this work.

---

*Corresponding author; turmine@ccr.jussieu.fr

[1] P. Pawlow, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **65**, 1 (1909).

[2] R. Defay, *Etude Thermodynamique de la Tension Superficielle* (Gauthier-Villars, Paris, 1934).

[3] R. Defay and I. Prigogine, *Surface Tension and Adsorption* (Longmans, Green, London, 1966), Chap. XVI, p. 269.

[4] D. Avnir and M. Jaroniec, Langmuir **5**, 1431 (1989).

[5] D. Avnir and P. Pfeifer, Nouv. J. Chim. **7**, 71 (1983).

[6] P. Pfeifer and D. Avnir, J. Chem. Phys. **79**, 3558 (1983).

[7] M. Jaroniec, X. Lu, R. Madey, and D. Avnir, J. Chem. Phys. **92**, 7589 (1990).

[8] Q. Jiang, S. Zhang, and M. Zhao, Mater. Chem. Phys. **82**, 225 (2003).

[9] M. K. Zayed, M. S. Hegazy, and H. E. Elsayed-Ali, Thin Solid Films **449**, 254 (2004).

[10] H. W. Sheng, K. Lu, and E. Ma, Nanostruct. Mater. **10**, 865 (1998).

[11] B. F. Borisov, A. V. Gartvik, F. V. Nikulin, and E. V. Charnaya, Acoust. Phys. **52**, 138 (2006).

[12] Q. Jiang, C. C. Yang, and J. C. Li, Mater. Lett. **56**, 1019 (2002).

[13] M. Zhang, M. Y. Efremov, F. Schiettekatte, E. A. Olson, A. T. Kwan, S. L. Lai, T. Wisleder, J. E. Greene, and L. H. Allen, Phys. Rev. B **62**, 10548 (2000).

[14] M. Wautelet, Phys. Lett. A **246**, 341 (1998).

[15] W. H. Qi and M. P. Wang, Mater. Chem. Phys. **88**, 280 (2004).

[16] Y. H. Wena, Z. Z. Zhu, R. Zhu, and G. F. Shao, Physica E (Amsterdam) **25**, 47 (2004).

[17] G. Guisbiers and M. Wautelet, Nanotechnology **17**, 2008 (2006).

[18] H. K. Christenson, J. Phys.: Condens. Matter **13**, R95 (2001).

[19] F. Delogu, J. Phys. Chem. B **109**, 21938 (2005).

[20] G. Bertsch, Science **277**, 1619 (1997).

[21] H. P. Cheng and R. S. Berry, Phys. Rev. A **45**, 7969 (1992).

[22] Z. Shi, P. Wynblatt, and S. G. Srinivasan, Acta Mater. **52**, 2305 (2004).

[23] K. K. Nanda, Eur. J. Phys. **19**, 471 (1998).

[24] S. J. Zhao, S. Q. Wang, D. Y. Cheng, and H. Q. Ye, J. Phys. Chem. B **105**, 12857 (2001).

[25] K. K. Nanda, Chem. Phys. Lett. **419**, 195 (2006).

[26] M. Turmine, A. Mayaffre, and P. Letellier, J. Phys. Chem. B **108**, 18980 (2004).

[27] T. L. Hill, Nano Lett. **1**, 273 (2001).

[28] I. Prigogine and R. Defay, *Thermodynamique Chimique* (Dunod, Paris, 1944), Tome I, p. 10.

[29] In physics, there are several developments of nonextensive thermodynamics using conventions in which the temperature is considered as nonintensive variable: S. Abe, S. Martinez, F. Pennini, and A. Plastino, Phys. Lett. A **261**, 534 (1998); R. Toral, Physica A **317**, 209 (2003).

[30] W. Ostwald, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **34**, 495 (1900).

[31] H. Freundlich, *Kolloidchemie* (Akademischer, Leipzig, 1909).

[32] D. Y. Kwok and A. W. Neumann, Adv. Colloid Interface Sci. **81**, 167 (1999).

[33] D. Y. Kwok and A. W. Neumann, Colloids Surf., A **161**, 31 (2000).

[34] K. Graf and H. Riegler, Langmuir **16**, 5187 (2000).

[35] N. X. Sun, H. Lu, and Y. C. Zhou, Philos. Mag. Lett. **76**, 105 (1997).

[36] Z. Zhang, J. C. Li, and Q. Jiang, J. Phys. D **33**, 2653 (2000).

[37] K. Lu and Z. H. Jin, Curr. Opin. Solid State Mater. Sci. **5**, 39 (2001).

[38] T. Ben David, Y. Lereah, G. Deutscher, R. Kofman, and P. Cheyssac, Philos. Mag. A **71**, 1135 (1995).

[39] W. H. Qi, Physica B **368**, 46 (2005).

[40] S. L. Lai, J. Y. Guo, V. Petrova, G. Ramanath, and L. H. Allen, Phys. Rev. Lett. **77**, 99 (1996).

[41] X. W. Wang, G. T. Fei, K. Zheng, Z. Jin, and L. D. Zhang, Appl. Phys. Lett. **88**, 173114 (2006).

[42] E. A. Olson, M. Y. Efremov, M. Zhang, Z. Zhang, and L. H. Allen, J. Appl. Phys. **97**, 034304 (2005).

[43] T. Unruh, H. Bunjes, K. Westesen, and M. H. J. Koch, Colloid Polym. Sci. **279**, 398 (2001).

[44] L. Grabaek, J. Bohr, E. Johnson, A. Johansen, L. Sarholt-Kristensen, and H. H. Andersen, Phys. Rev. Lett. **64**, 934 (1990).

[45] K. Chattopadhyay and R. Goswami, Prog. Mater. Sci. **42**, 287 (1997).

[46] Q. Jiang, Z. Zhang, and J. C. Li, Chem. Phys. Lett. **322**, 549 (2000).

[47] L. Zhang, Z. H. Jin, L. H. Zhang, M. L. Sui, and K. Lu, Phys. Rev. Lett. **85**, 1484 (2000).

[48] S. Auer and D. Frenkel, Phys. Rev. Lett. **91**, 015703 (2003).

[49] P. Letellier, A. Mayaffre, and M. Turmine, J. Colloid Interface Sci. (to be published).

[50] J. Belloni, Catal. Today **113**, 141 (2006).

[51] J. Belloni, M. O. Delcourt, and C. Leclere, Nouv. J. Chim. **6**, 507 (1982).

[52] R. Kubo, J. Phys. Soc. Jpn. **17**, 975 (1962).

[53] M. O. Delcourt and J. Belloni, Radiochem. Radioanal. Lett. **13**, 329 (1973).

[54] A. Henglein, Ber. Bunsenges. Phys. Chem. **81**, 556 (1977).

[55] M. D. Morse, Chem. Rev. (Washington, D.C.) **86**, 1046 (1986).

[56] E. Schumacher, Chimia **42**, 357 (1988).

[57] A. A. Shvartsburg and M. F. Jarrold, Phys. Rev. Lett. **85**, 2530 (2000).

[58] G. A. Breaux, R. C. Benirschke, T. Sugai, B. S. Kinnear, and M. F. Jarrold, Phys. Rev. Lett. **91**, 215508 (2003).

[59] G. A. Breaux, D. A. Hillman, C. M. Neal, R. C. Benirschke, and M. F. Jarrold, J. Am. Chem. Soc. **126**, 8628 (2004).

[60] K. Joshi, S. Krishnamurty, and D. G. Kanhere, Phys. Rev. Lett. **96**, 135703 (2006).

[61] T. L. Hill, Nano Lett. **1**, 111 (2001).

[62] T. L. Hill, Nano Lett. **1**, 159 (2001).