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Surface stress, surface tension and fusion temperature of very small condensed matter particles

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(30. VII. 1984)

In honor of Emanuel Mooser's 60th birthday

Abstract. Phenomenological thermodynamics can be used to understand the decrease of the melting temperature when the size of small systems decreases. The agreement between experimental results and the predictions is astonishingly excellent down to very small sizes (20 Å). A review is given here which includes not only the case of free particles but also the case of particles embedded in a matrix. The distinction between surface tension and surface stress is important when analyzing experimental results obtained on solid surfaces and on small particles. The existence of a surface induced pressure in anisotropic crystals depends on symmetries. A careful thermodynamical analysis is presented which precises the general conditions describing various equilibrium situations and the validity of Laplace type laws.

I. Introduction

From the point of view of statistical mechanics and thermodynamics, the phenomenon of fusion is studied in general for systems of large dimensions. In particular, a parameter describing the order at large distance vanishes when fusion takes place. In the case of very small systems, such a parameter cannot be defined. However, typical structures have been found experimentally in small particles. In some cases, these structures are characterized by the Bravais lattice of the corresponding large system (bulk) with eventually imperfections. In other cases, small particles show a quinary symmetry non existent in the corresponding large system. These particular shapes called MTP (Multi Twinned Particles) have been interpreted as resulting from 5 fcc tetrahedral crystals with a common edge (decahedra) or from 20 fcc tetrahedral crystals with a common apex (icosahedra [1, 2, 3, 4]. In all cases, fusion corresponds to the disappearance or at least to the non permanence of the atomic arrangement which results in particular in the absence of the characteristic diffraction pattern. Buffat [5], for example, studied the fusion of small gold MTP particles using the diffraction ring which corresponds locally to the (220) family of planes of a bulk fcc crystal. Other criteria of fusion have been mentioned. For example, Sambles et al. [6, 7] in the case of Gold particles used the variation of the evaporation rate at the melting point. Pepiatt [8] and Blackmann et al. [9] observed a sudden change of the external shape of metal particles. Devine et al. [10] in the case of bulk sodium and Sadeghi

et al. [11] in the case of small Na particles measured the increase of the conduction electron spin resonance (CESR) linewidth at the melting point.

The same diversity can be found in the theoretical approach of the problem. A description has been given elsewhere [39, 40]. In particular, the following examples can be given: the equality of the chemical potentials of the solid, liquid and vapor phases, the Lindemann criterion (fusion happens when the mean quadratic atomic displacement reaches a certain fraction of the nearest neighbour distance) and the sudden variation of a physical parameter at the fusion. Clearly, the phenomenon of fusion, in the case of small particles, can be understood without ambiguity. A phenomenological description will be given here which will be compared to our experimental results.

The distinction between surface tension (or surface free energy) and surface stress is important when analysing experimental results obtained on small particles. The derivation of the surface tension from the lattice contraction (measurements of the relative changes on the diffraction ring diameters) is inadequate for a solid. Effectively, the drop model commonly used [12, 13, 14, 15, 16] assumes that the crystal is isotropic, reducing the surface stress tensor to a hydrostatic pressure, and the shape of the small crystal to a sphere. The pressure is given by a Laplace law $\Delta p = 2\ \gamma/R$ where γ is the surface tension. It is clear that such a model does not take into account faceting of the microcrystals and the anisotropy of the bulk and surface stress tensors.

The virial of the surface forces which gives the volume change of a crystal [17, 18] has been calculated for a real crystal with a general faceted shape [19]. In particular, it has been found that the concept of pressure can still be defined inside a small crystal if a property called g symmetry is satisfied (relation between the geometry of the crystal and the surface stress g^s_{lm}). A thermodynamical analysis will be given here which precises the general conditions describing various equilibrium situations and the possible existence of a real pressure inside the solid particles.

II. Surface tension, surface stress and equilibrium conditions

The surface phase can be considered as a non autonomous two dimensional phase [12]. The work in the Gibbs equation is usually expressed as $\gamma\, dA$ where the surface tension coefficient γ corresponds to the increase of surface energy per unit area $\partial U^s/\partial A$ in the absence of surface deformations (the coefficient γ is also often written as σ). Such a description is adequate in the case of liquids where the excess surface stress immediately disappears because extra atoms migrate freely to the surface or away from it. In the case of solids, however, a distinction must be made between surface tension γ and surface stress g^s_{lm}, the later measuring the work required to deform the surface. In order to take this contribution into account, we have proposed to introduce explicitly the surface deformation variables ε^s_{lm} in the Gibbs equation [20]. The area A of the surface can be increased in two ways: i) by the increase dA^0 without structural change and ii) by the increase $dA^* = A\ \mathrm{Tr}\, d\varepsilon_{lm}$ due to the deformations. Accordingly, the work is equal to $\gamma\, dA^0 + \sum_{lm} A g^s_{lm}\, d\varepsilon^s_{lm}$. The Gibbs equations is then:

$$dU^s = T^s\, dS^s + \gamma\, dA + \sum_i \mu^s_i\, dm^s_i + \sum_{lm} A(g^s_{lm} - \gamma\, \delta_{lm})\, d\varepsilon^s_{lm} \tag{1}$$

T, S, μ_i and m_i are, as usual and respectively, the temperature, the entropy, the chemical potential and the adsorbed mass of the chemical component i. If only one chemical component is present, the position of the surface can be defined in such a way that $m_i^s = 0$ [12]. The energy function U^s is homogeneous and of first degree in the extensive variable $S^s A$ and m_i^s. Consequently, by Euler theorem: $U^s = T^s S^s + \gamma A + \sum_i \mu_i^s m_i^s$. In order for this latter expression to be compatible with equation (1), a Gibbs Duhem type of equation must be verified which, in the case of constant temperature and one chemical species, reduces to

$$g_{lm}^s = \gamma\,\delta_{lm} + \frac{\partial \gamma}{\partial \varepsilon_{lm}} \quad \text{or} \quad g^s = \tfrac{1}{2}\,\mathrm{Tr}\, g_{lm}^s = \frac{\partial}{\partial A}(\gamma A) \tag{2}$$

These well known expressions [21, 22] are obtained here in a new way. In the case of liquids, γ is independent of the strain tensor and $g_{lm}^s = \gamma\,\delta_{lm} = g^s\,\delta_{lm}$. It should be noted that, according to various studies [23, 24, 25], γ should be size independent down to approximately 10 Å.

A crystal is considered with general faceted shape surrounded by a liquid or a gaseous phase with which it can undergo exchange of mass by solution or evporation [12] (Fig. 1). The system is assumed to be adiabatic and characterized by constant volume and mass. Furthermore, to first order the volume changes dU^β are assumed to be equal to $A^\beta\, dh^\beta$ which leads to the relation:

$$A^\beta\, dh^\beta = \tfrac{1}{2} h^\beta\, dA^\beta \tag{3}$$

The expression of the entropy production near equilibrium is, according to the thermodynamics of irreversible process [26]:

$$\frac{dS^{\text{total}}}{dt} = \sum_m J_m X_m \geqslant 0 \tag{4}$$

where J_m and X_m are the generalized currents and conjugated forces. dS^{total}/dt is obtained from the Gibbs equations of the surface, fluid and solid phase. For these

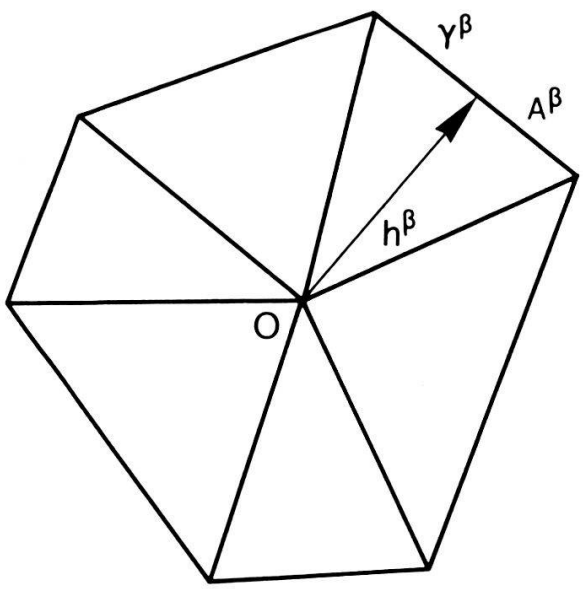

Figure 1

two latter phases:

$$dU^f = T^f\, dS^f - p^f\, dV^f + \sum_i \mu_i^f\, dm_i^f \tag{5}$$

$$dU^c = T^c\, dS^c + \sum_\beta \frac{\partial U^c}{\partial V^\beta}\, dV^\beta + \sum_i \mu_i^c\, dm_i^c \tag{6}$$

In these equations, p^f is the pressure existing in the fluid and $\sum_\beta (\partial U^c/\partial V^\beta)\, dV^\beta$ corresponds, in general, to the work in the crystal phase expressed in terms of the extensive variables V^β. Introducing equations (1), (5) and (6) in equation (4), the generalized currents are identified [20] as: the currents of energy, mass, area and deformation. The conjugated forces, according to the theory must be zero at total equilibrium. With the expected conditions of thermal equilibrium ($T_c = T_f = T_s$) and chemical equilibrium ($\mu_c = \mu_f = \mu_s$), one gets [20]:

$$-\left(p^f + \frac{\partial U^c}{\partial V^\beta}\right) = \frac{2\gamma^\beta}{h^\beta} \quad \text{and} \quad g_{lm}^\beta = \gamma^\beta\, \delta_{lm} \tag{7}$$

The diagonal form of g_{lm}^β implies that no deformations are present at the surface and therefore that the atoms can rearrange easily. This is certainly the case in liquids and solids at sufficiently high temperature or if defects of high mobility are present which should also be necessary in order to reach the chemical equilibrium. Another consequence of the diagonal form of g_{lm}^β is that the total virial of the surface forces is found to have a scalar form [19] and therefore that a pressure difference can be defined on both sides of the surface. The quantity $\partial U^c/\partial V^\beta$ is independent of β and can be interpreted as the effective pressure that should be applied to the corresponding bulk system in order to obtain the same deformations. From equation (7), the shape of the crystal is characterized by the well known Wulff relations [12]:

$$\frac{\gamma^\beta}{h^\beta} = \text{const.} \tag{8}$$

and a Laplace type law can be written: $p^e - p^f = 2(\sum_\beta \gamma^\beta A^\beta / \sum_\beta h^\beta A^\beta)$. In the case of fcc metals, the Wulff shape may be that of a regular cubooctahedra [1].

Assuming $\mu_i^c = \mu_i^f = \mu_i^s$ as well as constant mass and volume, other less restrictive conditions of equilibrium can be found, by minimizing the total free energy F (assuming constant temperature) or the total energy (assuming adiabaticity). If one chemical species is present, the equilibrium conditions are [20]:

$$-\left(p^f + \frac{\partial F^c}{\partial V^\beta}\right) = 2\,\frac{g^\beta}{h^\beta} \tag{9}$$

where g^β is defined by equation (2). If the virial of the surface forces is a scalar, a pressure difference can again be defined on both sides of the surface and the shape at equilibrium is governed by:

$$\frac{g^\beta}{h^\beta} = \text{const.} \tag{10}$$

Another Laplace type law can be written: $p^e - p^f = 2\,(\sum_\beta g^\beta A^\beta / \sum_\beta h^\beta a^\beta)$. These

relations are not restricted to isotropic crystals but are valid for any faceted crystal characterized by a scalar form of the virial. This is the case, for example [19], if the surface forces are perpendicular to the edges, for any direction, and if all planes having the same value g^β are distributed ('g symmetry') according to $\sum_\beta A^\beta \alpha_i^\beta \alpha_j^\beta = \text{const.}\ \delta_{ij}$ where α^β are the direction cosines of the normal to these β faces. Any regular polyhedron of cubic structure with g [111] $\neq$ g [100] satisfies the 'g-symmetry' and thus the equilibrium shape is described by equation (10).

In the more general case of several chemical species, a partial mechanical equilibrium is obtained [20] if the surface forces are, as before, perpendicular to the edges for any direction and if the surface increase is due to the deformations only: $dA^\beta = dA^{*\beta}$. A similar discussion leads to the equilibrium shape given by equation (10). In this case, however, dm_i^s and dm_i^c have a zero value and the equality of the chemical potentials is not necessary for the validity of equation (10).

All the equilibrium states described here are characterized by $-(\partial U^c/\partial V^\beta)$ or $-(\partial F^\beta/\partial V^\beta)$ independent of β which means that the deformations due to the presence of the surface are homogeneous. This is confirmed by experiments measuring the lattice contraction directly or indirectly [13, 15, 16]. The concept of effective pressure is phenomenological but does not correspond to a real physical pressure except in the case of isotropical systems and near the surfaces in the case of 'g-symmetry'. For example Solliard [27] has measured at room temperature, using electron diffraction, the lattice contraction of small Gold particles. The measurements verify a Laplace type law with an average value of the g^β equal to $g = (\sum_\beta g^\beta A^\beta / \sum_\beta A^\beta) = 3.1$ N/m. For the same type of Gold particles, Buffat [5] has determined the surface tension coefficient γ near fusion, $\gamma = 1.38$ N/m which leads to $\gamma = 1.84$ N/m at room temperature using the Eötvös coefficient $\partial\gamma/\partial T = -4.41\ 10^{-4}$ J/m^2 K [5]. Thus, the contribution $A(\partial\gamma/\partial A)$ has a value of order of 1.2 N/m in this case which shows that the surface is in a state of extension. In the case of silver particles of approximately 55 Å diameter [28], the lattice contraction also follows a Laplace type law with $g = 2.8$ N/m. Piuz et al. [29], from vapor pressure measurements as a function of size, have deduced at 567°C the value of the surface tension coefficient $\gamma = 1.4$ N/m. Taking into account the Eötvös coefficient $\partial\gamma/\partial T = -4.5\ 10^{-4}$ J/m^2 K, the value of γ at room temperature is $\gamma = 1.6$ N/m. Again the average value for $A(\partial\gamma/\partial A)$ is of order of 1.2 N/m corresponding to a state of extension of the surface. These results can be explained taking into account the MTP structure [3, 4]. In these structures all the faces are [111], have the same area and are distributed symmetrically. The total virial of the surface is scalar and relations (10) are verified for the external forces. Therefore, at equilibrium, one gets $\partial F^c/\partial V^\beta = \text{const.}$ independent of β and, accordingly, the elastic deformation of the crystal lattice necessary to allow the junction between the tetrahedra is uniform. The surface is in a state of large extension estimated to be 5% [27]. In the case of Platinum, normal fcc monocrystalline structure are observed down to approximately 30 Å [27]. The experimental results are interpreted in terms of a value of g slightly higher than γ which indicates that the surface is in a weak state of extension. Using a moire fringe method, Woltersdorf et al. [14] have measured Aluminium particles of 200 Å and 100 Å. Again, their conclusion is that the surface is in a state of extension. These examples show clearly the difference between surface stress and surface tension, the latter characterizing the total thermodynamical equilibrium state only.

III. Thermodynamical size effect

The chemical potential of a particle varies with its size. In order to study this effect, we have shown [30, 5] that, if the shape of the crystal follows the Curie Wulff relations, then the chemical potential can easily be expanded in a power series. Introducing the concept of equivalent pressure given by equation (8) one gets:

$$\begin{aligned}\mu(T,p) = \mu(T_0,p_0) &+ \frac{\partial\mu}{\partial T}(T-T_0) + \frac{\partial\mu}{\partial p}\left(p_{ext}+\frac{2\gamma}{h}-p_0\right)\\ &+\frac{1}{2}\frac{\partial^2\mu}{\partial T^2}(T-T_0)^2+\frac{1}{2}\frac{\partial^2\mu}{\partial p^2}\left(p_{ext}+\frac{2\gamma}{h}-p_0\right)^2\\ &+\frac{\partial^2\mu}{\partial p\,\partial T}\left(p_{ext}+\frac{2\gamma}{h}-p_0\right)(T-T_0)+\cdots\end{aligned} \tag{11}$$

The partial derivatives of the chemical potential can be expressed using the phenomenological equation valid in the volumic phases

$$-V\,dp_e + S\,dT + m\,d\mu = 0 \tag{12}$$

and the following phenomenological relations

isothermal compressibility $\quad x = \frac{1}{\rho}\frac{\partial\rho}{\partial p}$

linear expansion coef. $\quad \alpha = \frac{1}{3}\frac{\partial\rho}{\partial T}$

specific heat at constant pressure $\quad C_p = \frac{T}{m}\frac{\partial S}{\partial T} = T\frac{\partial S}{\partial T}$

latent heat of fusion $\quad L = \frac{T}{m}(S_L - S_S) = T(s_L - s_S)$

where the indices L and S characterize the liquid and the solid states respectively and $s = S/m$ the massic density of entropy. The expression for the chemical potential is then:

$$\begin{aligned}\mu(T,p) = \mu(T_0,p_0) - s(T-T_0) + \frac{1}{\rho}\left(p_{ext}+\frac{2\gamma}{h}-p_0\right) - \frac{Cp}{2T_0}(T-T_0)^2 -\\ -\frac{x}{2\rho}\left(p_{ext}+\frac{2\gamma}{h}-p_0\right)^2 + \frac{3\alpha}{\rho}\left(p_{ext}+\frac{2\gamma}{h}-p_0\right)(T-T_0)+\cdots.\end{aligned} \tag{13}$$

To first order, this equation becomes

$$\mu(T,p) = \mu(T_0,p_0) - s(T-T_0) + \frac{2\gamma}{\rho h} + \frac{p_{ext}-p_0}{\rho} \tag{13^{bis}}$$

If $p_{ext} = p_0$, equation (13) can be written in a more condensed form, always to

second order approximation:

$$\mu(T,p)=\mu(T_0,p_0)-s(T-T_0)+\frac{2\gamma}{\rho(h+h_0)}-\frac{Cp}{2T_0}(T-T_0)^2+$$
$$+\frac{3\alpha}{\rho}\left(\frac{2\gamma}{h}\right)(T-T_0)+\cdots \tag{14}$$

where

$$h_0=\gamma x \tag{15}$$

This quantity is often very small (<1 Å in the case of Au or Ag).

The fusion of small free particles

We assume here that, at the melting point, solid and liquid particles having the same mass exist simultaneously and are in equilibrium with the vapor phase (subscript g). The particles do not interact with the sample holder (see Fig. 2).

The fusion criterion is the chemical equilibrium

$$\mu_s=\mu_L=\mu_g \tag{16}$$

Figure 3 shows the phenomenon of fusion in the case of small particles. In this representation, the value of s_S is zero and the value of s_L is therefore equal to L/T_0. Naturally the reference temperature T_0 is taken as the fusion temperature of the bulk. If the vapor phase is a perfect gas, then the chemical potential follows the relation $\mu_g=\mu_\infty+(RT/M)\,\mathrm{Log}\,(p/p_\infty)$. With first order approximations for μ_s and μ_L, the equilibrium is characterized by a Gibbs–Thomson law:

$$p(h)=p_\infty(T)\exp\left(\frac{2\gamma M}{\rho RT}\right)\frac{1}{h} \tag{17}$$

According to this equation liquid and solid particles with the same mass should have the same vapor pressure. This law has been verified experimentally by Piuz [29] in the case of silver particles of order of 100 Å. The values found for γ_s are in good agreement with those measured in the case of bulk samples.

Buffat et al. [5] have solved equation (16) $\mu_s=\mu_L$ in the case of gold using the expression of the chemical potential (13) including the second order terms. Figure 4 shows both the result of the calculation and the experimental results of Buffat [5] and Sambles [6, 7].

Good agreement is found between experimental results and the calculations

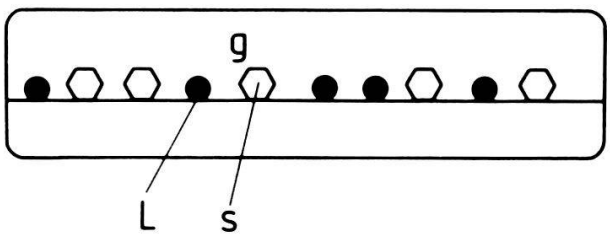

Figure 2
Chemical equilibrium between solid particles, liquid particles and vapor.

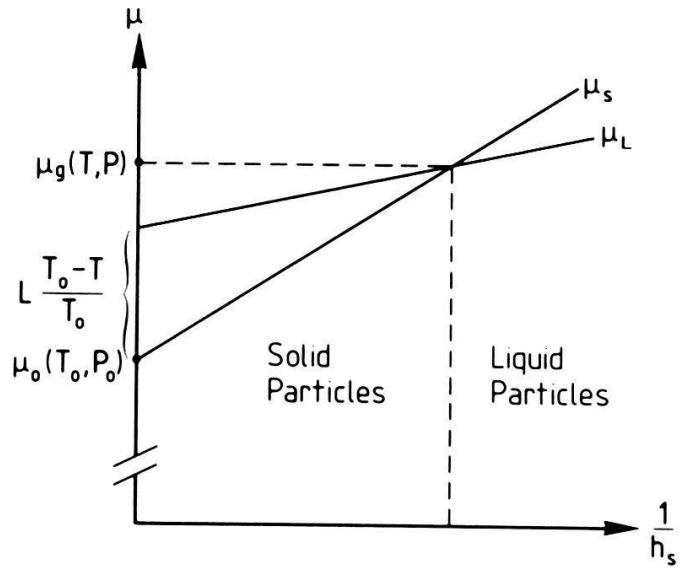

Figure 3
Chemical potentials according to equation (14) of solid and liquid particles as a function of the inverse of the radius h_s of the solid particles and at a given temperature $T < T_0$. (s_S has been taken as zero).

showing that phenomenological thermodynamics is capable of very good prediction down to astonishingly small sizes. If only the first order approximation is considered, the resolution of equation (16) is easy and the result is given by Pawlov's relation:

$$\frac{T_0 - T}{T_0} = \frac{2}{\rho_s L h_s}\left[\gamma_s - \gamma_L\left(\frac{\rho_s}{\rho_L}\right)^{2/3}\right] \tag{18}$$

This phenomenological equation predicts that the particles should be in a liquid state at any temperature if their size is smaller than a critical value.

$$h_s^c = \frac{2}{\rho_s L}\left[\gamma_s - \gamma_L\left(\frac{\rho_s}{\rho_L}\right)^{2/3}\right] \tag{19}$$

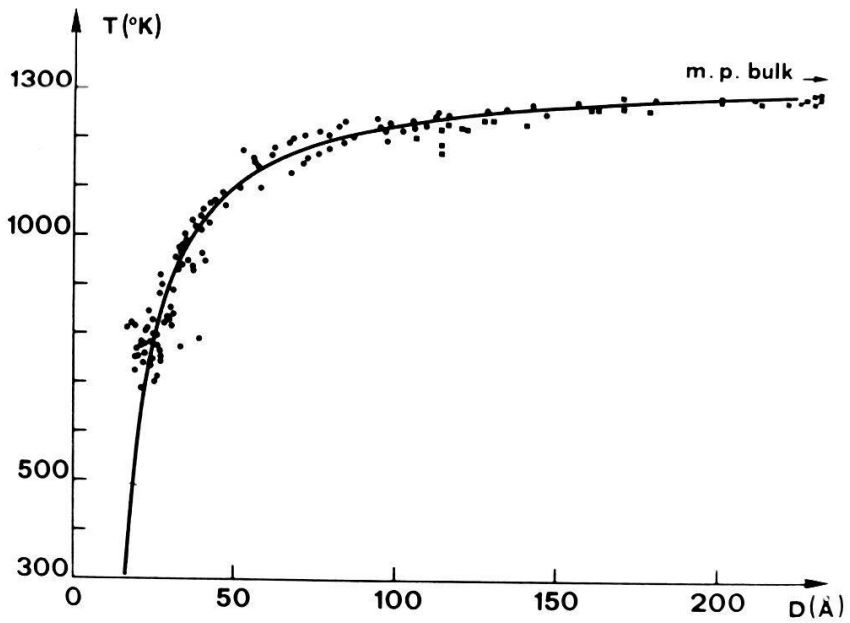

Figure 4
Experimental and theoretical values of the melting point temperature of gold particles.

If second order terms $h_{0L} = x_L \gamma_L$ and $h_{0s} = x_s \gamma_s$ are added, one gets:

$$h_s^c \cong \frac{2}{\rho_s L}\left[\gamma_s - \gamma_L\left(\frac{\rho_s}{\rho_L}\right)^{2/3}\right] - h_{0s} \tag{20}$$

where h_{0L} and h_{0s} have been assumed to verify the relation $h_{0L} \cong h_{0s}(\rho_s/\rho_L)^{1/3}$ in order to simplify the expression.

In the case of Au and most of the metals, h_s^c is found to be of the order of 1 Å. Indeed, thermodynamics does not apply for such sizes. This means that at low temperature, the particles keep an ordered structure down to very small clusters of atoms.

At first sight, substances characterized by larger values of h_s^c may exist. Friedel [31] has pointed out that this remark could explain the existence of an 'amorphous' phase in the case of small clusters, such a phase has been reported by Farges [32] in the case of Argon.

A good knowledge of certain phenomenological coefficients is very important in order to choose the substances that could show remarkable size effects. Unfortunately a certain lack of precise experimental results exists in this field; especially concerning the surface tension of solid and liquid phases, which constitutes undoubtedly a difficulty in the pursuit of investigations.

The fusion of small particle embedded in a solid matrix

Small particles embedded in a solid matrix can be prepared by following many different experimental procedures.

For example the X or UV irradiation of ionic crystals followed by appropriate heat treatments can precipitate point defects in the lattice and consequently produce small particles [38]. In such a case, the results obtained in the previous section are valid only if the solid or liquid particles can be considered as free inside a cavity. If not, interactions with the matrix must be introduced with the following main consequences: i) surface tensions γ_s and γ_L must be replaced by interfacial tensions γ_{sM} and γ_{LM} where the indice M stands for matrix. ii) an external pressure p_{ext} must be eventually introduced in order to take into account the pressure applied to the particles by the matrix.

Here we will assume that a 'membrane equilibrium' [33] exists across the matrix and, consequently, that the equilibrium is described as before by the equality of the chemical potentials of the solid and liquid particles of same mass. To first order approximation for μ:

$$\begin{aligned} \mu_S &= \mu(T_0, p_0) - s_S(T - T_0) + \frac{2\gamma_{SM}}{\rho_S h_S} + \frac{p_{\mathrm{ext}_S} - p_0}{\rho_s} \\ \mu_L &= \mu(T_0, p_0) - s_L(T - T_0) + \frac{2\gamma_{LM}}{\rho_L h_L} + \frac{p_{\mathrm{ext}_L} - p_0}{\rho_L} \end{aligned} \tag{21}$$

A generalized Pawlow equation is obtained, neglecting the vapor pressure p_0:

$$\frac{T_0 - T}{T_0} = \frac{2}{L\rho_s h_s}\left[\gamma_{SM} - \gamma_{LM}\left(\frac{\rho_S}{\rho_L}\right)^{2/3}\right] + \frac{1}{L}\left[\frac{p_{\mathrm{ext}_S}}{\rho_S} - \frac{p_{\mathrm{ext}_L}}{\rho_L}\right] \tag{22}$$

As an example, the following case can be considered: the solid fills exactly and

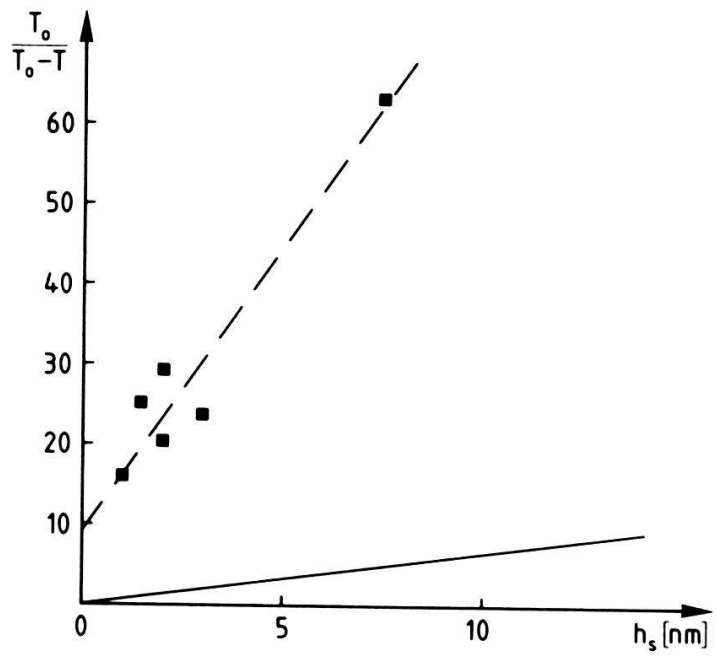

Figure 5
Representation of $(T_0 - T(h_s))/T_0$ as a function of the size h_s in the case of Na particles. The solid line corresponds to the prediction of equation (18) with the values of the parameters mentioned in the text. The ----- line corresponds to the best fit for the experimental values measured in a NaN_3 matrix.

without stress a cavity in a rigid matrix and therefore, the fusion is characterized by constant volume. In such a case, $p_{ext_S} = 0$ and $p_{ext_L} = (1/x_L)(\rho_S - \rho_L/\rho_S)$ where the values of the volumic masses are here those of the free phases. In the case of Sodium and near T_0, $\rho_s = 0.9552 \times 10^3$ kg/m^3, $\rho_s = 0.9275 \times 10^3$ kg/m^3 and $x = 1.9 \times 10^{-10}$ m^2/N [34, 37] which leads to $p_{ext_L} = 1.5 \times 10^8$ N/m^2. This value exceeds by far the limit of elasticity of any matrix and thus p_{ext_L} must be smaller.

The fusion of Na particles in a matrix of NaN_3 has been observed using the conduction electron spin resonance technique (CESR). When the temperature increases, the linewidth increases and, at the fusion, a discontinuity is observed [35, 36]. The fusion temperature has been found experimentally (Fig. 5) to follow a $T_0/(T_0 - T) = ah_S$ law rather than a $T_0/(T_0 - T) = ah_S/(1 - abh_S)$ where

$$b = \frac{1}{L}\frac{p_{ext_L}}{\rho_L} \quad \text{and} \quad a = \frac{L\rho_S}{2}\frac{1}{\left[\gamma_{SM} - \gamma_{LM}\left(\frac{\rho_s}{\rho_L}\right)^{2/3}\right]}.$$

As a consequence, the pressure excited by the matrix on the particles appears to be zero. The value of the coefficient $[\gamma_{SM} - \gamma_{LM}(\rho_S/\tau_L)^{2/3}]$ deduced from this experiment is $\sim 10^{-2}$ N/m. Using the values of $\gamma_S = 0.290$ N/m and $\gamma_L = 0.202$ N/m generally accepted in the literature [34, 37] a value of $\sim 10^{-1}$ is found. This result indicates that γ_{SM} is only slightly higher than γ_{LM} which is reasonable considering that the preparation procedures of the Na particles involves a heat treatment at temperature above the fusion point of the metal.

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