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Surface stress of isotropic solids under irreversible conditions

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Abstract

Surface stress of isotropic solids is discussed when irreversible mechanisms in the interfacial solid/vapour region occur. When stretching the surface of a sample, even at mechanical equilibrium and in the absence of relaxation, local mobility of atoms and defects can be induced on a thin layer adjacent to the surface. Our thermodynamic formulation takes into account the variation of the surface free energy with the chemical composition of this thin underlayer. Such interfacial region is called non-autonomous phase, as previously designated for fluids by Defay and Prigogine. The theory developed here permits to a new interpretation of the surface stress. This quantity depends on the variation of the surface free energy with the elastic surface deformation weighted by the relative deformation of the crystal, the aspect ratio of the underlying sheets and the chemical composition. *To cite this article: A. Sanfeld, A. Steinchen, C. R. Chimie 6 (2003).*

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Résumé

Suivant l'intensité de la contrainte imposée à la surface d'un solide, des déformations irréversibles peuvent apparaître, même en l'absence de toute relaxation et loin du régime plastique. La contribution dissipative liée au réarrangement des espèces est due à la perte d'autonomie de la surface. Il en découle une expression généralisée de la tension de surface tenant compte de la variation de l'énergie libre de surface avec la déformation élastique de surface factorisée par la déformation relative du cristal, le rapport d'aspect et la composition chimique à la fois de la surface et de la sous-couche sollicitée. *Pour citer cet article : A. Sanfeld, A. Steinchen, C. R. Chimie 6 (2003).*

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1. Introduction

There have been many discussions on the physical significance of the difference between surface free energy, surface tension and surface stress of solids. The major cause of controversy is the widespread misinterpretation and confusion of these quantities. Typical confusions encountered are: (*i*) mixing up surface free energy per unit area and surface stress; (*ii*) surface tension (a concept restricted to liquid phases) and sur-

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face stress; (*iii*) static or dynamic surface stress. In a previous paper [1], we recall their meaning in the frame of the Shuttelworth formulation in terms of the variation of the surface free energy with the surface elastic deformation, classically defined by the relative surface variation [2]. This presentation clears up certain obscure points in Gibbs and Rice presentation [3], but it is only valid for reversible work of deformation. Surface stress is generally defined as a reversible work per area to stretch a solid surface elastically while the surface tension of a liquid, often mixed up with the surface free energy, is the reversible work per unit area to create a surface. Alternatively, it is generally admitted that the surface stress is the energy involved in the creation of a unit deformed surface at constant sites and the surface tension is the energy involved to create a surface in maintaining constant the deformation. Although there have been many discussions about the physical significance of the difference between these quantities, important controversies remain still a topical question. Fundamental macroscopic and microscopic aspects were analysed by many authors on the role of stress [4–6]. For the reader who is interested in detailed theoretical and experimental developments, a brief survey is presented in our previous paper [1]. All these presentations assume the existence of reversible states during and after the stretch of the surface. There is, however, a domain for which, according to its magnitude, the stretch applied on the surface might result in irreversible mechanisms taking place at the surface and in the underlying crystal. Although the amplitude of the constraint imposed remains behind the limit of relaxation effects as well as behind the limit of plasticity, the removal of such constraint might not preserve the relative initial position of atoms and defects. In order to introduce this new concept of surface stress, we shall first develop a revisited Laplace law taking into account the variation of the surface free energy with the elastic deformation and the chemical composition of the surface and its underlying layer. From this formulation we derive a general definition of the surface stress.

2. A revisited Laplace formulation in relation with the lack of autonomy of the interphase

Due to the asymmetry of the interactions and in the absence of any imposed constraint, the region separating two immiscible phases is a quasi-continuous inhomogeneous thin layer [3,7,8]. In this surface region, the matter density as well as the lattice distance varies quasi continuously, but very sharply, along a coordinate normal to the surface. Gibbs introduced a geometrical dividing surface (superscript σ), which is always taken parallel to the surface of tension. This model in which the thickness of the interface is, in effect, taken as zero, is used in place of the real system. The quantity of matter n_m^σ, attributed to an arbitrary dividing surface may then be positive or negative, and, on division by the area of the dividing surface, A, we may define a quantity called Gibbs adsorption, $\Gamma_m = \dfrac{n_m^\sigma}{A}$. Now, the Gibbs' model is mechanically equivalent to the real system, only when the position of the dividing surface is identical to the surface of tension (surface characterized by zero couple of forces). As well known, most particle surfaces are rough and asperities as small as 1–2 nm can significantly lower or raise the position of the dividing surface. Hence, it is necessary to choose quantities whose values are invariant whatever the position of the dividing surface, or at least, are such that small errors in locating the surface lead to relatively small errors. The relative adsorption is a quantity with this property. The same reasoning prevails for all thermodynamic quantities such as the free energy. For the sake of simplicity, we are modelling here the behaviour of a two-component system, the metal atoms, m, and either vacancies, v, or impurities. The choice of one of the components as reference substance of zero adsorption allows to define the Gibbs relative excesses of matter, $\Gamma_{m[v]}$, and of surface free energy, $f_{[v]}^\sigma = \dfrac{F^\sigma}{A}$ [9]. Now, when a deformation is imposed to the surface of the solid, according to the duration and magnitude of the constraint, an irreversible transfer process of atoms, vacancies and point defects might occur in a very thin quasi-continuous region underneath the surface of tension, usually called sublayer (sb), whose composition at its bottom reaches that of the bulk of the solid [1,11]. Due to the interactions between the atoms in the surface and in the sublayer, the global surface free energy F^σ varies with the chemical composition of the sublayer. For this reason, the surface is a non-autonomous phase. The irreversible process which occurs in the stretched isotropic crystal lies both in the transfer of the atoms

between the surface and the sublayer and to a rearrangement of the interfacial region. According to the fluctuations theory, all these processes, even for very small objects in the size limit ≥ 100 Å, enter the frame of a macroscopic description of the physicochemical properties.

We now take into account the conservation law for the atoms

$$n_{\mathrm{m}}^{\sigma} + n_{\mathrm{m}}^{\mathrm{sb}} + n_{\mathrm{m}}^{\mathrm{s}} + n_{\mathrm{m}}^{\mathrm{v}} = \text{Const} \tag{1}$$

where the solid (s) is an infinite reservoir and the vapour phase (v) an infinite sink so that, from Eq. (1), in the steady non-equilibrium state,

$$dn_{\mathrm{m}}^{\sigma} = - dn_{\mathrm{m}}^{sb} \tag{2}$$

Taking into account (2), the sets of independent extensive are now for a zero adsorption of the vacancies:

$$(V^{\mathrm{sb}}, A, n_{\mathrm{m}}^{\mathrm{sb}}, n_{\mathrm{v}}^{\mathrm{sb}}) \text{ or } (V^{\mathrm{sb}}, A, n_{\mathrm{m}}^{\sigma}, n_{\mathrm{v}}^{\mathrm{sb}}) \tag{3}$$

This choice of independent variables finds its justification in the fact that, in the open system considered here, an atom is not always simply exchanged with a vacancy, but much more complex mechanisms of exchange may occur: interstitial diffusion, interactions between vacancies and dislocations, very different diffusion time scales of atoms and vacancies, fusion and collective movement of species, interactions with point defects and impurities. A classical procedure in thermodynamics allows us to replace also the set of extensive variables $(V^{\mathrm{sb}}, A, n_{\mathrm{m}}^{\sigma}, n_{\mathrm{v}}^{\mathrm{sb}})$ by the set of intensive variables $(\Gamma_{\mathrm{m}}, C_{\mathrm{v}}^{\mathrm{sb}})$, where $C_{\mathrm{v}}^{\mathrm{sb}} = \dfrac{n_{\mathrm{v}}^{\mathrm{sb}}}{V^{\mathrm{sb}}}$.

The total free energy $F = F^{\mathrm{sb}} + F^{\sigma} + F^{\mathrm{s}} + F^{\mathrm{v}}$ is a function of all the independent variables $F(T, V^{\mathrm{s}}, V^{\mathrm{sb}}, V^{\mathrm{v}}, A, n_{\mathrm{m}}^{\mathrm{sb}}, n_{\mathrm{v}}^{\mathrm{sb}}, n_{\mathrm{m}}^{\mathrm{v}}, n_{\mathrm{m}}^{\mathrm{s}}, n_{\mathrm{v}}^{\mathrm{s}})$. As the bulk of the solid (s) and the vapour (v) phases are respectively infinite reservoir and sink, on differentiating this function with the composition of the sublayer, maintaining constant T, the volumes $V^{\mathrm{s}}, V^{\mathrm{sb}}, V^{\mathrm{v}}$, the area A, the number of atoms in the vapour and solid phases, $n_{\mathrm{m}}^{\mathrm{v}}, n_{\mathrm{m}}^{\mathrm{s}}$, the number of vacancies in the solid, $n_{\mathrm{v}}^{\mathrm{s}}$, and in the sublayer, $n_{\mathrm{v}}^{\mathrm{sb}}$, we obtain

$$\frac{\partial F}{\partial n_{\mathrm{m}}^{\mathrm{sb}}} = \frac{\partial F^{\mathrm{sb}}}{\partial n_{\mathrm{m}}^{\mathrm{sb}}} + \frac{\partial F^{\sigma}}{\partial n_{\mathrm{m}}^{\mathrm{sb}}} \tag{4}$$

The quantity $\dfrac{\partial F}{\partial n_{\mathrm{m}}^{\mathrm{sb}}}$ is called the complete chemical potential, $\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}}$, while $\dfrac{\partial F^{\mathrm{sb}}}{\partial n_{\mathrm{m}}^{\mathrm{sb}}} = \mu_{\mathrm{m}}^{\mathrm{sb}}$ is the classical local

chemical potential. The last term $\dfrac{\partial F^{\sigma}}{\partial n_{\mathrm{m}}^{\mathrm{sb}}}$ describes the lack of autonomy of the surface. This quantity accounts for the functional character of capillary quantities like does the theory of the second gradient developed since the pioneering work of van der Waals.

As the interactions between the vacancies with the metal atoms in the sublayer are larger than with the atoms in the surface, we may neglect, as a first approximation, the variation of F^{σ} with $n_{\mathrm{v}}^{\mathrm{sb}}$. Hence,

$$\frac{\partial F}{\partial n_{\mathrm{v}}^{\mathrm{sb}}} = \frac{\partial F^{\mathrm{sb}}}{\partial n_{\mathrm{v}}^{\mathrm{sb}}} \tag{5}$$

where the quantity in the l.h.s is the complete chemical potential $\bar{\mu}_{\mathrm{v}}^{\mathrm{sb}}$ and the quantity in the r.h.s is the classical chemical potential $\mu_{\mathrm{v}}^{\mathrm{sb}}$.

Eqs. (4) and (5) may finally be written respectively:

$$\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}} = \mu_{\mathrm{m}}^{\mathrm{sb}} + \frac{\partial F^{\sigma}}{\partial n_{\mathrm{m}}^{\mathrm{sb}}} \tag{6}$$

$$\bar{\mu}_{\mathrm{v}}^{\mathrm{sb}} = \mu_{\mathrm{v}}^{\mathrm{sb}} \tag{7}$$

In a non-equilibrium state, $\bar{\mu}_{\mathrm{m}}^{\sigma} \neq \bar{\mu}_{\mathrm{m}}^{\mathrm{sb}}$, while the equilibrium is ruled by the equality of the complete chemical potentials. The equality of chemical potentials is not realized when the stretch of the surface creates an irreversible rearrangement of the mobile atoms and vacancies.

Now, making use of (2) one may rewrite (6) by a simple change of variables at constant area:

$$\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}} = \mu_{\mathrm{m}}^{\mathrm{sb}} - \frac{\partial f_{[v]}^{\sigma}}{\partial \Gamma_{\mathrm{m}[v]}} \tag{8}$$

As the elastic deformation, $\epsilon = \delta A/A$, depends on the surface concentration, $\gamma_{\mathrm{m}[v]}$, maintaining constant the total numbers of metal atoms $n_{\mathrm{m}} = n_{\mathrm{m}}^{\sigma} + n_{\mathrm{m}}^{\mathrm{sb}}$ in the surface and the sublayer, we get:

$$\left(\frac{\partial f_{[v]}^{\sigma}}{\partial \Gamma_{\mathrm{m}[v]}} \right)_{T, C_{\mathrm{v}}^{\mathrm{sb}}} = \left(\frac{\partial f_{[v]}^{\sigma}}{\partial \epsilon} \right)_{T, n_{\mathrm{m}}, C_{\mathrm{v}}^{\mathrm{sb}}} \left(\frac{\partial \epsilon}{\partial \Gamma_{\mathrm{m}[v]}} \right)_{T, n_{\mathrm{m}}, C_{\mathrm{v}}^{\mathrm{sb}}} \tag{9}$$

From Eqs. (8) and (9), the complete chemical potential is seen to be:

$$\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}} = \mu_{\mathrm{m}}^{\mathrm{sb}} - \left(\frac{\partial f_{[v]}^{\sigma}}{\partial \epsilon} \right) \left(\frac{\partial \epsilon}{\partial \Gamma_{\mathrm{m}[v]}} \right) \tag{10}$$

where, for the sake of simplicity, we omit the subscripts T, n_{m}, C_{v}.

Consider, in a first approach, homogeneous transformations in a crystal. The pressure tensor reduces to

a scalar quantity and the variation of the volume, dV, includes creation and elastic deformation effects. Hence, the Gibbs–Duhem law reads for the sublayer phase at constant T:

$$\mathrm{d}p^{\mathrm{sb}} = C_{\mathrm{m}}^{\mathrm{sb}}\,\mathrm{d}\mu_{\mathrm{m}}^{\mathrm{sb}} + C_{\mathrm{v}}^{\mathrm{sb}}\,\mathrm{d}\mu_{\mathrm{v}}^{\mathrm{sb}} \qquad (11)$$

where variations of chemical potential include changes of internal and elastic energy.

Remark. Let us justify the validity of the Gibbs–Duhem relation for a class of irreversible processes in the linear domain (transport, diffusion, adsorption, deformations, re-arrangements, etc.). It is well known that this relation is valid for reversible processes. In this particular case, the removal of the imposed constraint leads to the instantaneous vanishing of the deformation. Local equilibrium is instantaneously established in comparison with the elastic deformation, dissipative phenomena arising after the establishment of the elastic regime. On the other way, by loading or bending a crystal, dissipative effects may appear due to atomic rearrangements inside the material. Friction, reorientation, displacements of defects (vacancies, dislocations, microfissures, etc.) occur and may lead to strong modifications of the internal tensions, as for example relaxation of deformations (delayed elasticity) or relaxation of constraints (flow regime). More complex situations arise when reaching a critical threshold of the constraint. Indeed, in suppressing or in maintaining constant the constraint, deformation has not stopped but proceeds in time. This behaviour is called plastic regime out of the Hookean domain. Already one century ago, Kelvin showed that a remnant modification of materials such as gold or copper might be due to compression. Indeed, voids are always present in many materials and volumetric plasticity thus exists, which dissipates the elastic energy by a relaxation process. All these irreversible processes induce a common global combined movement of the material, which by definition refers to thermodynamic- and mechanical-non-equilibrium states. In a number of other cases, the mechanical equilibrium state is however established very quickly in comparison with the thermodynamic processes. Then, virtually at the beginning of the irreversible process studied, such state is reached. For instance, when chemical or thermal diffusion phenomena occur, one can safely suppose that the state of mechanical equilibrium (in which the acceleration vanishes) is quickly realized to a sufficient ap-

proximation. Such a regime can also occur in elastic isotropic solids when the surface is stretched by external forces or by phase transformations, such as solidification from the melt or evaporation. Also chemical constraints, such as diffusion of oxygen from the vapour phase at high temperature restores the elastic behaviour of some metals up to the threshold of fracture. This is due to the interstitial positioning of the oxygen atoms in the metallic lattice.

In all these cases, the response of the system to the applied mechanical or chemical constraints does not instantaneously restore the initial thermodynamic state, even at the mechanical equilibrium. Hence, irreversible mechanisms appear at the surface and in a thin region adjacent to the surface. In these situations, the sublayer may still be described in terms of the same variables as at equilibrium, i.e. the Gibbs–Duhem relation remains valid.

Inserting Eqs. (7) and (10) in (11) and taking, for the sake of simplicity, a mean value in space of the concentration $\langle C_{\mathrm{m}}^{\mathrm{sb}}\rangle$ in the quasi-continuous sub-layer, we get:

$$\mathrm{d}p^{\mathrm{sb}} - C_{\mathrm{m}}^{\mathrm{sb}}\,\mathrm{d}\!\left(\frac{\partial f_{[\mathrm{v}]}^{\sigma}}{\partial \varepsilon}\right)\!\left(\frac{\partial \varepsilon}{\partial \Gamma_{\mathrm{m}[\mathrm{v}]}}\right)$$
$$= \mathrm{d}\!\left(p^{\mathrm{sb}} - \langle C_{\mathrm{m}}^{\mathrm{sb}}\rangle\!\left(\frac{\partial f_{[\mathrm{v}]}^{\sigma}}{\partial \varepsilon}\right)\!\left(\frac{\partial \varepsilon}{\partial \Gamma_{\mathrm{m}[\mathrm{v}]}}\right)\right)$$
$$= C_{\mathrm{m}}^{\mathrm{sb}}\,\mathrm{d}\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}} + C_{\mathrm{v}}^{\mathrm{sb}}\,\mathrm{d}\bar{\mu}_{\mathrm{v}}^{\mathrm{sb}} \ (12)$$

Integrating Eq. (12) on the thickness, e, of the sublayer and taking into account the fact that the deformation vanishes at the lower boundary of the layer, we may then define an extended capillary pressure that we call $\bar{\mathrm{p}}^{\mathrm{sb}}$. At the bottom of the layer: $p^{\mathrm{sb}} = \bar{p}^{\mathrm{sb}}$, $\mu^{\mathrm{sb}} = \bar{\mu}^{\mathrm{sb}}$; on the top: $\bar{p}^{\mathrm{sb}} = \bar{p}^{\mathrm{sb}}$, $\bar{\mu}^{\mathrm{sb}} = \bar{\mu}^{\mathrm{sb}}$. This extended overpressure accounts for the irreversible interaction with the surface during the stretch (see [10], Appendix II):

$$\bar{p}^{\mathrm{sb}} = p^{\mathrm{sb}} - \langle C_{\mathrm{m}}^{\mathrm{sb}}\rangle\!\left(\frac{\partial f_{[\mathrm{v}]}^{\sigma}}{\partial \varepsilon}\right)\!\left(\frac{\partial \varepsilon}{\partial \Gamma_{\mathrm{m}[\mathrm{v}]}}\right)$$
$$= \int_{\mu_{\mathrm{m}}^{\mathrm{sb}}}^{\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}}} C_{\mathrm{m}}^{\mathrm{sb}}\,\mathrm{d}\bar{\mu}_{\mathrm{m}}^{\mathrm{sb}} + \int_{\mu_{\mathrm{v}}^{\mathrm{sb}}}^{\bar{\mu}_{\mathrm{v}}^{\mathrm{sb}}} C_{\mathrm{v}}^{\mathrm{sb}}\,\mathrm{d}\bar{\mu}_{\mathrm{v}}^{\mathrm{sb}} \ (13)$$

This extended pressure directly leads to an extended Laplace formulation. Indeed, on subtracting the pressure in the vapour phase (13), we get:

$$\bar{p}^{\mathrm{sb}} - p^{\mathrm{v}} = (p^{\mathrm{sb}} - p^{\mathrm{v}}) - \langle C_{\mathrm{m}}^{\mathrm{sb}}\rangle\!\left(\frac{\partial f_{[\mathrm{v}]}^{\sigma}}{\partial \varepsilon}\right)\!\left(\frac{\partial \varepsilon}{\partial \Gamma_{\mathrm{m}[\mathrm{v}]}}\right)$$
$$(14)$$

3. Surface stress with dissipative mechanisms

Let us apply Eq. (14) at the surface of tension, reminding that $f^\sigma_{[v]}$ is invariant whatever the position of the dividing surface. As shown in our previous paper [1], for an isotropic sphere of radius R_0 in the non-stretched reference state, the capillary pressure $2 S^s_T/R_0$ obtained from the variation of the standard chemical potential associated to the change of curvature by an equilibrium displacement reads:

$$\frac{2 S^s_T}{R_0} = \frac{\Delta \mu^{0sb}_m}{v^0_m} = \phi [p^{sb} - p^v] \qquad (15)$$

in which the factor $\phi = \left[1 - \dfrac{\chi^{sb}(p^{sb} + p^v)}{2} \right]$ includes the compressibility coefficient χ, v^0_m is the standard molar volume.

An extended capillary pressure, $2S/R$, in the stretched state, is then defined by:

$$\frac{2 S}{R} = \phi [\bar p^{sb} - p^v] \qquad (16)$$

in which $R = R_0 + \delta R$ with $\delta R << R$ and $\varepsilon = 2\, \delta R/R_0$.

Consequently

$$\frac{2 S}{R} = \frac{2 S^s_T}{R_0} - \phi \langle C^{sb}_m \rangle \left(\frac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \left(\frac{\partial \varepsilon}{\partial \Gamma_{m[v]}} \right)$$

$$= \frac{2 S^s_T}{R_0} - \phi \frac{2\langle C^{sb}_m \rangle}{R_0} \left(\frac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \left(\frac{\partial\, \delta R}{\partial \Gamma_{m[v]}} \right) (17)$$

This quantity, S, located at R, we have called surface stress, has thus the same meaning as S^s_T, but with an additional contribution due to the elastic deformation of the surface $\left(\dfrac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \left(\dfrac{\partial \varepsilon}{\partial \Gamma_{m[v]}} \right)$. Equilibrium states belong to autonomous surfaces and in such cases $\dfrac{\partial F^\sigma}{\partial n^{sb}_m} = 0$. In contrast with equilibrium, non-equilibrium states are described in terms of irreversible processes due to diffusion of species and deformation of the lattice. Such situations lead to a lack of autonomy of the surface, characterized by the derivative $\dfrac{\partial F^\sigma}{\partial n^{sb}_m}$ or finally by $\left(\dfrac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \left(\dfrac{\partial \varepsilon}{\partial \Gamma_{m[v]}} \right)$.

Let us now assume as a reasonable approximation, that ε is a decreasing linear function for small variations of $\Gamma_{m[v]}$ (an increase of $\Gamma_{m[v]}$ enhances the surface rigidity and thus diminishes its elasticity).

Eq. (17) then reads:

$$\frac{2 S}{R} = \frac{2 S^s_T}{R_0} + \phi \langle C^{sb}_m \rangle \frac{\varepsilon}{\Gamma_{m[v]}} \left(\frac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \qquad (18)$$

and, similarly for a cubic crystal of finite size λ:

$$\frac{4 S}{\ell} = \frac{4 S^s_T}{\ell_0} + \phi \langle C^{sb}_m \rangle \frac{\varepsilon}{\Gamma_{m[v]}} \left(\frac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \qquad (19)$$

Indeed, as shown by Kern and Müller [11] in the restricted case of equilibrium, the origin of the over-pressure lies in the finite size λ via the surface stress. In order to interpret Eqs. (18) and (19) in terms of aspect ratio and composition of the sublayer, we shall now transform the factor $\langle C^{sb}_m \rangle \dfrac{\varepsilon}{\Gamma_{m[v]}}$. Suppose a uniform stretch applied to the whole surface of a sphere. This corresponds to a homogeneous compression. Such process creates a slightly deformed spherical sublayer of mean radius $<R>$ different from R_0 and of thickness e in which the composition is different from that of the bulk phase. We may then write $V^{sb} = 4 \pi \langle R \rangle^2 e$, therefore:

$$\langle C^{sb}_m \rangle = \frac{n^{sb}_m}{4 \pi \langle R \rangle^2 e} \; ; \; \varepsilon = \frac{\delta A}{A_0} = \frac{2\, \delta R}{R_0} \; ; \; \Gamma_{m[v]} = \frac{n^\sigma_m}{4 \pi R_0^2} \qquad (20)$$

and for a cubic crystal:

$$\langle C^{sb}_m \rangle = \frac{n^{sb}_m}{\langle \ell \rangle^2 e} \; ; \; \varepsilon = \frac{\delta A}{A_0} = \frac{2\, \delta \ell}{\ell_0} \; ; \; \Gamma_{m[v]} = \frac{n^\sigma_m}{\ell_0^2} \quad (21)$$

Hence, as a first approximation, we may write

$$\frac{R_0^2}{R_0 \langle R \rangle} \simeq \frac{1}{R} \text{ and } \frac{\ell_0^2}{\ell_0 \langle \ell \rangle^2} \simeq \frac{1}{\ell}$$

From Eqs. (18)–(21), we obtain finally the extended capillary pressure, respectively for the sphere and for the cubic crystal:

$$S = S^s_T + \frac{\delta R}{e} \frac{n^{sb}_m}{n^\sigma_m} \phi \left(\frac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \text{ (sphere)} \qquad (22)$$

$$S = S^s_T + \frac{1}{2} \frac{\delta \ell}{e} \frac{n^{sb}_m}{n^\sigma_m} \phi \left(\frac{\partial f^\sigma_{[v]}}{\partial \varepsilon} \right) \text{ (cube)} \qquad (23)$$

The quantities $\dfrac{\partial R}{e} \simeq \dfrac{\langle R \rangle}{e} \dfrac{\delta R}{R_0}$ and $\dfrac{1}{2} \dfrac{\delta \ell}{e} \simeq \dfrac{1}{2} \dfrac{\langle \ell \rangle}{e} \dfrac{\delta \ell}{\ell_0}$ compare the small deformations $\left(\dfrac{\delta R}{R_0}, \dfrac{\delta \ell}{\ell_0} \right)$ of the crystal to the aspect ratios $\left(\dfrac{e}{\langle R \rangle}, \dfrac{e}{\langle \ell \rangle} \right)$ of the sublayer. The ratio $\dfrac{n^{sb}_m}{n^\sigma_m}$ is the compositional weighting factor of the

variation of surface free energy with the elastic surface deformation. Since Orowan deduction [12], that the stress in the surface could be one of compression, the sign and magnitude of the term $\left(\dfrac{\partial f^{\sigma}_{[v]}}{\partial \varepsilon}\right) = A_0 \left(\dfrac{\partial f^{\sigma}_{[v]}}{\partial A}\right)$ is still the subject of controversy. By numerical simulation, it has been recently shown [13] that, in the absence of constraint, the heterogeneous surface layer of a small crystal of Al is composed of eight atomic sheets: the two first ones being in compression and the next six in tension. Under an imposed deformation, the two first layers are modified differently from the six next ones.

Finally, let us compare Eqs. (22)–(23), and the Shuttelworth formulation, $S^{\mathrm{Sh}} = \dfrac{\partial F^{\sigma}}{\partial A} = f^{\sigma} + A\,\dfrac{\partial f^{\sigma}}{\partial A}$. In (22)–(23) and according to (15)–(18)), the surface stress is defined by the jump of pressure across the surface in full agreement with the Laplace law of capillarity. In the Shuttelworth formulation, however, the dependence of the pressure appears indirectly through the deformation term $A\,\dfrac{\partial f^{\sigma}}{\partial A}$. Indeed, by a classical change of variables, this last term is equal to $-\Gamma_{\mathrm{m}}\,\mu^{\sigma}_{\mathrm{m}}$, where it is assumed by the author that $\mu^{\sigma}_{\mathrm{m}}$ is the equilibrium chemical potential. On the other hand, f^{σ}, which refers to the creation of the surface, depends on pressure only by the elastic energy through the compressibility, a very small contribution. A more detailed description of the present theory is now in press [10].

Acknowledgements

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