Journal of Nuclear Materials 505 (2018) 127–133

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

# On the Laplace-Young equation applied to spherical fluid inclusions in solid matrices

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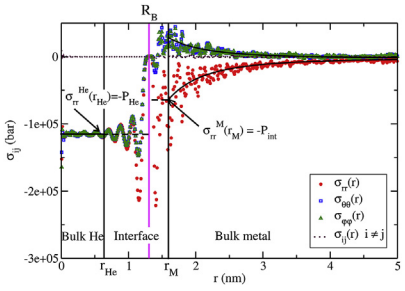
## HIGHLIGHTS

- A continuum theory of surfaces is used to analyse a set of molecular dynamics results obtained on helium/steel systems.
- The $\Gamma$ factor from the Laplace-Young equation applied to the helium/steel systems was calculated using two methods.
- $\Gamma$, which is a surface stress like quantity, exhibits a non-linear dependency on the helium/steel interface strain.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 6 December 2017
Received in revised form
28 March 2018
Accepted 28 March 2018
Available online 31 March 2018

*Keywords:*
Interface
Helium bubble
Austenitic steel
Molecular dynamics

## ABSTRACT

A continuum theory of surfaces is successfully applied to analyse a set of molecular dynamics results obtained on systems consisting of nanosize fluid bubbles trapped in a solid matrix. The equations of this theory supplied with molecular dynamics data allowed calculating the $\Gamma$ factor from the Laplace-Young equation as applied to systems of industrial interest, such as the helium bubbles that form along the ageing of some austenitic steel components of the nuclear reactors. The $\Gamma$ factor was found to have a non-linear dependency on the helium/steel interface strain. These findings are in contradiction with the implicit assumption made in some published literature considering $\Gamma$ as a constant.



## 1. Introduction

The last years have seen an increased interest in the theoretical study of nanosize fluid inclusions (bubbles) trapped in various solid matrices [1–7]. In most studies, the Laplace-Young equation, as established for the fluid/fluid systems, is also used for the fluid/solid ones:

$$P_B = \frac{2\Gamma}{R_B} + P_S \tag{1}$$

Here, $P_B$ is the pressure of the fluid in the bubble, $R_B$ is the bubble radius, $P_S$ is the pressure applied by the solid matrix on the bubble surface and the $\Gamma$ factor is often identified with the surface free energy of the fluid/solid interface (for example, see Refs. [1–5]). However, for some authors [8–10], the $\Gamma$ factor from the Laplace-Young equation applied to systems containing solid surfaces is a surface stress rather than a surface free energy.

As shown in Ref. [11], the surface stress, which is an excess quantity, can be expressed through a second rank tensor, the

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https://doi.org/10.1016/j.jnucmat.2018.03.051
0022-3115/

surface excess stress tensor. In a spherical coordinate system, its components are calculated as follows:

$$\gamma_{ij} = \frac{1}{R_0^2}\left[\int_{r_\alpha}^{R_0}\left[\sigma_{ij}(r) - \sigma_{ij}^{\alpha}(r)\right]r^2 dr + \int_{R_0}^{r_\beta}\left[\sigma_{ij}(r) - \sigma_{ij}^{\beta}(r)\right]r^2 dr\right] \quad i,j = r,\theta,\varphi \tag{2}$$

In equation (2), $r_\alpha$ and $r_\beta$ are the $\alpha$ and $\beta$ side limits of the $\alpha/\beta$ interface, $\sigma_{ij}(r)$ are the components of the stress tensor in the interface and $\sigma^{\alpha,\beta}{}_{ij}(r)$ are the corresponding components of the stress tensor in the $\alpha$ and $\beta$ bulk phases extrapolated to the geometrical dividing surface. The geometrical surface position $r = R_0$ is chosen in an arbitrary way within the interface ($r_\alpha < R_0 < r_\beta$). If the system has a spherical symmetry and, in addition, the bulk phases $\alpha$ and $\beta$ are homogeneous, the following equations hold:

$$\begin{aligned}
&\forall r \in [r_\alpha, R_0) \quad \sigma_{\theta\theta}^{\alpha}(r) = \sigma_{\varphi\varphi}^{\alpha}(r) = \sigma_{rr}^{\alpha}(r) = \sigma_{rr}^{\alpha}(R_0) = \sigma_{rr}^{\alpha}(r_\alpha) = ct_1 \\
&\forall r \in \left[R_0, r_\beta\right] \quad \sigma_{\theta\theta}^{\beta}(r) = \sigma_{\varphi\varphi}^{\beta}(r) = \sigma_{rr}^{\beta}(r) = \sigma_{rr}^{\beta}(R_0) = \sigma_{rr}^{\beta}\left(r_\beta\right) = ct_2 \\
&\forall r \quad \sigma_{ij}^{\alpha,\beta}(r) = \sigma_{ij}(r) = 0 \quad i \neq j
\end{aligned} \tag{3}$$

where $ct_1$ and $ct_2$ are constant with respect to $r$.

The definition of the surface stress by equation (2) also introduces a normal component, $\gamma_{rr}$, suggesting a three dimension aspect of the surface stress. As can be seen from equation (2), every component of the surface excess stress tensor is a function of $R_0$, the position of the geometrical surface in the interface. For a spherical interface, the function $\gamma_{rr}(R_0)$ takes the following form [11]:

$$\gamma_{rr}(R_0) = \frac{R_0\left[\sigma_{rr}^{\beta}(R_0) - \sigma_{rr}^{\alpha}(R_0)\right]}{3} + \frac{C}{R_0^2} \quad where \quad C < 0 \tag{4}$$

The shape of the function $\gamma_{rr}(R_0)$ expressed by equation (4) shows that there is always a geometrical surface position $R_0 = R_s$ such that $\gamma_{rr}(R_s) = 0$. For this point, the geometrical surface is called the surface of tension and the surface excess stress tensor becomes bi-dimensional [11].

Starting from the general condition of mechanical equilibrium at a curved interface between the phases $\alpha$ and $\beta$, the author of reference [11] also derived a vector form of the Laplace-Young equation in a generalized curvilinear coordinate system. This equation is applicable to all forms of curved interfaces irrespective of the nature of the $\alpha$ and $\beta$ bulk phases (solid or fluid). If a spherical coordinate system is used and the system has a spherical symmetry, the generalized Laplace-Young vector equation reduces to the following scalar form:

$$\sigma_{rr}^{\alpha}(R_0) - \sigma_{rr}^{\beta}(R_0) = -\frac{2\Gamma}{R_0} \tag{5}$$

In equation (5), $\sigma_{rr}^{\alpha}(R_0)$ and $\sigma_{rr}^{\beta}(R_0)$ are the radial components of the stress tensor in the bulk phases $\alpha$ and $\beta$ applied to the $\alpha$ side ($r = r_\alpha$) and the $\beta$ side ($r = r_\beta$) faces of the interface, extrapolated to the geometrical surface ($r = R_0$). In the case where the $\alpha$ and $\beta$ bulk phases are homogeneous, equations (3) apply and the extrapolation gives: $\sigma_{rr}^{\alpha}(R_0) = \sigma_{rr}^{\alpha}(r_\alpha)$ and $\sigma_{rr}^{\beta}(R_0) = \sigma_{rr}^{\beta}(r_\beta)$. $\Gamma$ is calculated using the following relation:

$$\Gamma = \frac{\Gamma_{\theta\theta} + \Gamma_{\varphi\varphi}}{2} \tag{6}$$

where $\Gamma_{\theta\theta}$ and $\Gamma_{\varphi\varphi}$ are obtained from the tangential components of the stress tensor:

$$\Gamma_{ii} = \frac{1}{R_0}\left[\int_{r_\alpha}^{R_0}\left[\sigma_{ii}(r) - \sigma_{ii}^{\alpha}(r)\right]rdr + \int_{R_0}^{r_\beta}\left[\sigma_{ii}(r) - \sigma_{ii}^{\beta}(r)\right]rdr\right] \quad i = \theta,\varphi \tag{7}$$

The physical quantities $r_{\alpha,\beta}$, $\sigma_{ii}(r)$, $\sigma^{\alpha,\beta}{}_{ii}(r)$ and $R_0$ from equation (7) have the same meaning as in equation (2). However, the surface stresses they define, $\Gamma_{ii}$ and $\gamma_{ii}$, are different, with one exception [11], when the geometrical surface is chosen to coincide with the surface of tension ($R_0 = R_s$). Only for this case, when the surface excess stress tensor becomes bi-dimensional, the $\Gamma$ factor from the Laplace-Young equation is equal with $\gamma^m$, the average of the tangential components of the surface excess stress tensor:

$$\begin{aligned}
&\Gamma_{\theta\theta}(R_s) = \gamma_{\theta\theta}(R_s) \qquad \Gamma_{\varphi\varphi}(R_s) = \gamma_{\varphi\varphi}(R_s) \\
&\Gamma(R_s) = \frac{\Gamma_{\theta\theta}(R_s) + \Gamma_{\varphi\varphi}(R_s)}{2} = \frac{\gamma_{\theta\theta}(R_s) + \gamma_{\varphi\varphi}(R_s)}{2} = \gamma^m(R_s)
\end{aligned} \tag{8}$$

In the present work, the concepts and relations of the continuum theory of surfaces (CTS) from Ref. [11] previously introduced are used to analyse a set of molecular dynamics results obtained on systems where the size of one of the phases is of the order of nanometer. For the molecular dynamics study, one chose the particular case of helium bubbles confined in a face centered cubic (fcc) FeNiCr alloy at compositions similar to AISI-316 austenitic steels: the $\alpha$ phase is the helium (He) and the $\beta$ phase is the metal (M).

This work has also an applied objective, since it provides two methods allowing to calculate the $\Gamma$ factor for fluid/solid interfaces in systems of industrial interest. In particular, predicting the evolution and the properties of the helium bubbles in AISI-316 austenitic steels is crucial for understanding the ageing phenomena affecting some steel components of the nuclear reactors.

The paper is structured as follows: Section 2 presents the models and methods employed in this study. The first part of Section 3 gives a characterization of the helium/steel interface on the basis of molecular dynamics results. In the second part of Section 3, the concepts and equations of CTS are employed to analyse the molecular dynamics data and to calculate the $\Gamma$ factor from the Laplace-Young equation. Section 4 gives a summary of the results of this study.

## 2. Models and methods

### 2.1. Models for the helium/steel systems

The calculations presented in this paper were carried out using 3D periodic boundary conditions. The pattern for the periodical model was built starting from a supercell of 31 × 31 x 31 fcc elementary cells. The fcc sites of this supercell were randomly filled with Fe, Ni and Cr atoms in order to create a model reproducing the AISI-316 alloy which has a composition (in weight %) of 12% Ni, 17.5% Cr and 70.5% Fe [12] and displays a homogeneous distribution of the components (Fe, Ni, Cr) in the matrix [13]. The resulting cubic supercell contains 83385 Fe atoms, 13512 Ni atoms and 22267 Cr atoms.

This perfect fcc supercell was then relaxed through molecular