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ScienceDirect

Acta Materialia 89 (2015) 14–21

Acta MATERIALIA

www.elsevier.com/locate/actamat

The capillarity equation at the nanoscale: Gas bubbles in metals

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Received 15 July 2014; revised 9 January 2015; accepted 21 January 2015

Abstract—We investigate the modifications to the Young–Laplace capillarity equation needed to describe nanoscale gas bubbles embedded in metals, scale at which the finite width of the interface region cannot be neglected. We focus in particular on the case of He in Fe. Using both, the concept of Tolman's length that provides a curvature dependence for the interface energy, and a new equation of state for He at the nanoscale that accounts for interface effects (see Caro et al., 2013), we derive an expression to predict pressure, and from it density and the amount of He in nanoscale bubbles. We find that conditions for equilibrium are found for values of pressure or density at variance by a factor of ~ 2 compared to the traditional way of using the capillarity equation and a bulk He EOS.

Keywords: Capillarity equation; Helium bubbles Fe; Nanoscale effects; Tolman's length

1. Introduction

Capillarity, an old concept developed by Young and Laplace in the early 19th century [1,2], plays an essential role in many different fields of science and engineering. In the traditional definition, capillarity is the tendency of wetting liquids to be drawn into the confined space of a narrow tube. In a wider definition, it includes the phenomenon of enhanced pressure of a droplet due to the constrictive surface tension force. The concept in fact involves all phenomena in which two phases are separated by a curved interface, and as such it is of interest in biology, geology, physical chemistry, micro- and nanotechnology, and tribology, and for a diversity of applications such as electrospray, nano-fountain pen writing, capillarity bridges, and in natural sciences to understand certain animal locomotion and plants nutrition; for a review see van Honschoten et al. [3].

Most of the studies in the literature, as well as the discussion that follows in this Section, consider the problem of capillarity between fluid phases. When two fluids, in mutual mechanical equilibrium, are separated by a spherical interface of radius R, the pressure of the fluid inside, p^{α}, differs from that of the fluid outside, p^{β}. If the interface is assumed to be of zero thickness, the condition for mechanical equilibrium provides a simple relation between p^{α} and p^{β}, which is known as the Kelvin relation [4].

$$\Delta P = p^{\alpha} - p^{\beta} = \frac{2\gamma_{\infty}}{R} \tag{1}$$

where γ_{∞} is the surface energy for a flat ($R \to \infty$) surface. This method for treating surface tension is simple and useful but it is of an approximate nature from the molecular view point, for the structure of the fluid undergoes not a discontinuous but a progressive modification across the actual interface. When looking at the micro and nano scales, the effects of the finite width of the interface. i.e. the existence of interfacial forces, or the molecular structure of matter, cannot be neglected and need to be solved explicitly; by doing so fundamentally new phenomena appear, making capillarity at the nanoscale a vivid subject of research today.

As early as in 1949, based solely on thermodynamic arguments, Tolman showed that the Kelvin relation could be not valid for small fluid bubbles. He proved departures from the equation for the case of one-component two-phase systems of liquid bubbles in equilibrium with their vapor [5]. He introduced what is since then known as Tolman length δ that gives a correction term to the surface energy, namely:

$$\gamma_R \simeq \gamma_{\infty} / \left(1 + \frac{\delta}{R}\right) \tag{2}$$

with δ in the range of intermolecular distances. Higher order terms in $1/R^n$ are to be expected for small radii, and were discussed in Tolman's original paper.

A vast literature covers diverse aspects of the problem. Among them Ono and Kondo, and Rowlinson and Widow authored a review and a book, respectively on the molecular theory of capillarity that are classics in the field [6,7]. As examples of recent work, we mention the contributions by Marchand et al. [8], and Style et al. [9–12] on the contact

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http://dx.doi.org/10.1016/j.actamat.2015.01.048

angle that a liquid drop makes on a soft substrate, which appears different from that predicted by Neumann's law [13], the complex scaling behavior of indentation of soft surfaces by adhesion forces [10] and the capillarity driven instabilities in soft solids [14–16].

Using computational modeling at the atomic scale, several papers look at details of the interface region and evaluate pressures and densities for nanoscale bubbles or drops, mainly on Lennard-Jonnes model systems [17–24]. Of particular interest to us is the work by Thompson et al. [25] who evaluate density profiles and put to test the concept of Tolman's length for the surface energy. They report density and pressure profiles that transition from the liquid to the vapor phases in a region (the interface) of the order of the interaction range of the potential, as expected from Tolman's theory.

Despite the abundant literature in this subject, we are not aware of a similar level of effort to describe gas bubbles embedded in metals, which are expected to behave in a similar qualitative way, although with some differences, as we shall see below, given the fact that the solid containing the bubble is able to sustain shear. Such bubbles are a relevant microstructure feature in irradiated materials where noble gases such as He, Xe, and Kr appear as a result of nuclear reactions. Their presence is usually a nuisance as they affect mechanical and thermal properties in dramatic ways [26,27]. Chemically inert, these gases have a exceedingly low solubility in solids and a strong tendency to precipitate heterogeneously at defects such as dislocations, grain boundaries or precipitate interfaces.

To our knowledge, there has been no connection between the studies of nanoscale effects in bubbles, mostly in the field of colloid physics as briefly reviewed above, and the field of bubbles embedded in materials under irradiation. Support to this conclusion comes from the fact that the usual treatment of noble gas bubbles in materials, as for example given in the standard reference book by Was, 'Fundamentals of Radiation Materials Science' [28], uses Eq. (1) in combination with either an ideal gas or a van der Waals equation of state for the gas, to predict equilibrium and kinetic processes.

In this work we seek to establish this connection by bringing knowledge well established in colloidal physics to solid state physics and determine scaling effects for nanoscale He bubbles in Fe, aiming at providing a quantitative evaluation of the departure from the Young–Laplace Eq. (1) as we enter the nanoscale, and establishing the conditions under which a bubble is said to be in equilibrium with its environment.

Motivation for our study comes from our recent work on the structure of these nanoscale bubbles [29]. There we evaluate the pressure inside a He bubble and show that, in contrast to the common assumption for macroscale bubbles, that pressure (the trace of the stress tensor) is constant, for He bubbles at the nanoscale this picture is no longer valid. P and density ρ can no longer be defined as global quantities related by an equation of state, EOS, for the fluid, but they become functions of position, because the bubble develops a core–shell structure originated in the atomic scale dimensions of the interface, in a similar way as reported by Thompson for Lennard-Jones fluids [25]. The range of the metal–gas interaction defines the width δ of the interface, which for the He–Fe system studied, is $\delta \sim 0.4$ nm, implying that bubbles in the range of 1 nm diameter are almost entirely affected by this interface effect, creating a radial pressure profile that within a distance δ from the interface, is not constant in the fluid, nor zero in the metal, as the theory of the Eshelby inclusion, which is valid beyond the interface, would predict [30].

The paper is organized as follows: we first calculate via direct computer simulations, the pressure, density and number of particles in equilibrium bubbles. Then we apply the Tolman's theory to fit these results with an R-dependent surface energy. We then develop an EOS for nanoscale bubbles, and finally, we compare our predictions with results of simulations. A discussion section finalizes the work.

2. Results

2.1. Equilibrium bubbles and the capillarity equation

A usual way to estimate the amount of gas in a bubble embedded in a metal is to assume mechanical and thermodynamic equilibrium, i.e., the gas pressure equals the capillarity force $P = 2\gamma/R$, Eq. (1) and the chemical potential for vacancies far from the bubble and at its surface are equal; under this condition there is no driving force for vacancies to be preferentially emitted or absorbed by the bubble. The amount of gas in the bubble can then be estimated using Eq. (1) just from its size, the surface energy of the host matrix, and an EOS for the fluid relating P, T and density.

The first question we address is a quantification of the discrepancy between the prediction of Eq. (1) and the result of an atomic scale calculation of equilibrium bubbles. We study the case of He in Fe using empirical potentials and molecular dynamics. For details on the simulations see Ref. [29]. A bubble in (mechanical) equilibrium is a bubble containing exactly the amount of gas that produces no perturbation to the elastic fields (stress and strain) of the surrounding metal atoms, at a distance larger that the interface width of ~ 0.4 nm mentioned above. To find this condition we use a simulation cell consisting of a spherical Fe crystal with five concentric shell regions, all but the inner-most thickness equal to the cut-off of the potential r_{cut}. The inner-most region is the bubble of varying radius, where He sits.

The sample is created with the lattice constant of Fe at the chosen target temperature. It is embedded in vacuum. Atoms in the outermost shell of this iron ball are frozen in place. Traveling inward, this shell is followed by another shell with moving Fe atoms that form a buffer zone between the frozen atoms and the so called integration zone, the shell of moving Fe atoms where stress calculations are performed. The integration region is followed by a second buffer region which screens from the interactions with He gas atoms. The innermost shell contains the He gas in a spherical cavity.

The precise characterization of the elastic fields in a spherical domain with frozen boundary conditions can be found in Ref. [31], but here we are only interested in equilibrium bubbles, situation where these fields are zero, which greatly simplifies the analysis. If instead of the gas in the cavity, we place a perfect crystal of Fe, the pressure and all the elements of the stress tensor in the integration region become zero, within numerical accuracy and thermal noise. Now, placing in the inner zone gas atoms at some varying densities, the condition of zero pressure in the integration zone will be obtained for a gas density corresponding to