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Compressibility, the measurement of surface tension, and particle size in molecular or nuclear matter

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Abstract

It is shown that the interface shrinkage resulting from the capillary pressure difference between both sides of a curved interface is the product of a "standard shrinkage" $\kappa\gamma$ (κ is the isothermal compressibility, γ the interfacial tension) by a dimensionless factor that depends only on the shape of the sample of matter under study. The behaviour of the standard shrinkage in the critical domain shows that it cannot be a measure of the thickness of the liquid–vapour interface in that domain. The standard shrinkage of classical liquids somewhat above triple point is usually near to $0.048 v_c^{1/3}$ (v_c is the critical molecular volume); exceptions to this rule are discussed. The variation of the standard shrinkage along the liquid–vapour coexistence curves of water and argon is presented; the effect of the interface shrinkage on the measured surface tension of liquids can become important within about 15% of the critical temperature. The standard shrinkage of solids is less than that of the corresponding liquids, and is of no consequence when measuring the surface tension of solids. The standard shrinkage of the nuclear fluid is $0.23\ \text{fm} = 0.09 v_c^{1/3}$. The saturation density of infinite nuclear matter is about 9% less than its value in atomic nuclei, and a term proportional to $A^{1/3}$ (A is the mass number) must be added to the nuclear binding energy formula.

Keywords: Surface energy; Thermodynamics of surfaces and interfaces; Critical exponents; Nuclear matter; Nuclear binding energies and masses

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1. Introduction

Classically, the surface tension γ (in N/m) is considered to be the excess of free enthalpy (Gibbs free energy) per unit area of properly defined interface.

Egelstaff and Widom [1a] showed that the capillary overpressure between the inside and the outside of a spherical drop of radius R leads to a radius decrement $\Delta R = -\frac{2}{3}\kappa\gamma$, κ being the isothermal compressibility (in Pa^{-1}), which is independent of R. They also showed that the product $\kappa\gamma$, which we propose to call "standard shrinkage," is at triple point proportional to a hard-core molecular diameter, or alternatively to the thickness of the liquid–vapour interface. This second interpretation has been developed by various authors, notably N.H. March, using mostly refinements of the van der Waals mean-field theory (see [1b, Section 12.5]).

In this article we intend to show that, when one measures surface tension in non-planar geometries, compressibility leads to a volume contribution which can be of comparable magnitude to the surface term, or even (near the critical point) overwhelming, from which ensues a potentially large error in the measurement of surface tension.

We shall apply our results in turn to vapours, liquids, solids, and to the nuclear fluid (see [2] and [3] for a presentation of the relevant forces), and discover that the standard shrinkage is directly comparable with molecular or nucleonic size.

2. Surface and volume terms that result from the creation of an interface

We shall restrict our study to pure substances so as not to be hindered by the problems of variable composition and of adsorption.

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We shall also assume, except in Section 3.3, that the curvature of the interface is small enough so that the thermodynamical properties of the interface differ little from those of the corresponding infinite planar interface, and for the "surface of tension" (defined by a nil bending moment for the system of tangential forces) to differ little from the "surface of zero mass" (defined by the overall mass of the sample and by its density well inside the interface).

At a constant temperature, and inside of a medium that remains at a constant pressure p_e, the amount of work needed in order to reversibly create an interface of area $\mathcal{A}$ wrapped around a sample of volume V, initially at p_e, can be written as follows, if we neglect terms that are relatively at most of the order of the curvature of the interface:

$$W = \mathcal{A}\gamma - (\Delta V)p_e - V(\Delta p), \tag{2.1}$$

where γ is the interfacial tension according to its classical definition (surface excess of free enthalpy per unit area of the surface of tension) and ΔV is the volume variation of the sample that results from the capillary pressure difference Δp between the inside and the outside of the interface.

We shall moreover restrict our study to the three one-dimensional sample shapes: sphere, quasi-infinite circular cylinder, and quasi-infinite parallel plate. Let us call n the exponent of the enclosed volume as a function of the coordinate (radius). These three shapes correspond respectively to:

(a) $n = 3$: a drop of negligible weight or, conversely, a spherical bubble (maximum bubble pressure method to measure the surface tension) or the ascent of a fluid within a capillary tube.
(b) $n = 2$: the measurement of surface tension by the stretch of a weighted wire or, conversely, the ascent of a fluid between parallel plates.
(c) $n = 1$: the stretching of a plane capillary film.

Laplace's theorem tells us that the capillary pressure difference between the inside and the outside of the interface is

$$\Delta p = \frac{n-1}{R}\gamma, \tag{2.2}$$

R being the radius of the sphere, that of the circular cylinder, or (for instance) the half-thickness of the parallel plate. Let us now call κ the isothermal compressibility of the sample of matter under study:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\mathrm{T}}. \tag{2.3}$$

Strictly speaking, κ is not $\kappa(p_e)$, but an average over pressures that vary from p_e to $(p_e + \Delta p)$, for which $\kappa(p_e + \Delta p/2)$ should usually be an excellent approximation. However, for a solid, or even a liquid not too near the critical state, the corresponding difference in κ should be very small, even when the curvature of the interface is not vanishingly small.

If we neglect higher-order terms, we find that

$$\frac{\Delta V}{V} = -\kappa\frac{n-1}{R}\gamma. \tag{2.4}$$

Assuming that the sample contracts isotropically,[1] there comes

$$\frac{\Delta R}{R} = \frac{1}{3}\frac{\Delta V}{V} = -\frac{n-1}{3}\frac{\kappa\gamma}{R}, \tag{2.5}$$

$$\Delta R = -\frac{n-1}{3}\kappa\gamma. \tag{2.6}$$

We therefore reach the conclusion that the interface shrinkage resulting from the capillary pressure difference is, at constant temperature and external pressure, and assuming $\kappa \simeq \kappa(p_e)$ (see above), independent of the size of the sample of matter under study. It is moreover proportional to a geometrical factor which is of course 0 for a parallel plate, where the capillary pressure difference is nil, and which is worth $1/3$ for a circular cylinder, and $2/3$ for a sphere (like in [1a]), where the effect is maximum. We have already called $\kappa\gamma$ the "standard shrinkage."[2]

Again neglecting higher-order terms, one may write

$$W + V(\Delta p) = \mathcal{A}\gamma - \mathcal{A}(\Delta R)p_e = \mathcal{A}\gamma', \tag{2.7}$$

$$\gamma' = \gamma + \frac{n-1}{3}(\kappa\gamma)p_e \tag{2.8}$$

$$= \gamma\left(1 + \frac{n-1}{3}\kappa p_e\right). \tag{2.9}$$

Note that the $+$ sign should be replaced by a $-$ sign in (2.8) and (2.9) in the case of negative curvature, the shrinkage becoming then an expansion ($\Delta R > 0$).

What is measured when stretching a plane capillary film is therefore indeed the surface excess of free enthalpy per unit area of interface ($\gamma' = \gamma$ for $n = 1$) but what is measured when a fluid ascends between parallel plates or within a capillary tube is $\gamma' < \gamma$. This difficulty is not mentioned in the recent textbook by Adamson and Gast [5], which reviews in much detail the various methods for measuring surface or interface tension.

Let us return to the case of positive curvature and consider a bubble of vapour that behaves like a perfect gas, in which case the following holds to an excellent approximation:

$$\kappa = \frac{1}{p_e + \Delta p/2} = \frac{1}{p_e + (n-1)\gamma/2R}, \tag{2.10}$$

$$\frac{n-1}{3}\kappa p_e = \frac{1/3}{1/(n-1) + \gamma/2Rp_e} \xrightarrow[R\to\infty]{} \frac{n-1}{3}. \tag{2.11}$$

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[1] If the length of the quasi-infinite circular cylinder was instead fixed, one would find that $\Delta R/R = \frac{1}{2}\Delta V/V$ and therefore $\Delta R = -\frac{1}{2}\kappa\gamma$, instead of $-\frac{1}{3}\kappa\gamma$ from (2.6). If the span of the quasi-infinite parallel plate was instead fixed, one would find that $\Delta R/R = \Delta V/V$, and therefore $\Delta R = 0$ like in (2.6).

[2] $\kappa\gamma$ also serves to calculate the decrease in the capillary increase of the vapour pressure of a drop of radius R, which is due to the compressibility of the drop; see [4, formula (15.24)].