

Note on the existence of negative pressures

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The mechanical equilibrium of two fluids separated by a curved interface requires the existence of a hydrostatic pressure, Δp between them; this is given by the Laplace equation:

$$\Delta p = \gamma C$$

Here, γ is the interfacial tension between the fluid and C is the mean curvature of the interface, defined as $1/R_1 + 1/R_2$ where R_1 and R_2 are the principal radii of curvature. For a spherical surface of radius R , we have $R_1 = R_2 = R$, and the Laplace equation takes the familiar form:

$$\Delta p = 2\gamma/R$$

An important feature of the Laplace equation is that it defines a pressure difference. The curvature must therefore be given an algebraic sign in order to give the correct sense to Δp . the convention adopted is such that the pressure is higher on the 'concave' side of the interface than on the 'convex' side. Thus, the pressure is higher inside a gas bubble than in the surrounding liquid. (A consequence is that small bubbles, or fine particles, show an enhanced solubility).

By the same token, a wetting liquid in a fine capillary exists under a lower pressure than the surrounding gas, since the meniscus formed is concave towards the gas. Indeed, combining the Laplace equation with the expression for the gravitational head in a vertical tube leads immediately to the familiar equation of capillary rise:

$$h = \frac{2\gamma \cdot \cos \theta}{r \cdot \rho \cdot g}$$

(The relationship between the meniscus radius R , the capillary radius r and the contact angle θ is implied by Figure 1.)

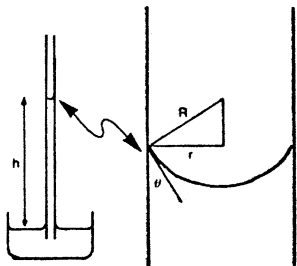


Fig 1

The Laplace equation underlies the fluid penetration method of pore size measurement described by Mr. Ranger (see e.g. equation (4) of his paper), and also methods based on static capillary suction for wetting liquids, and intrusion of non-wetting liquids like mercury. when the contact angle exceeds 90° , $\cos \theta$ becomes negative and Δp changes sign, so that excess pressure is needed to force mercury into the pores.

For the case of a wetting liquid in equilibrium with a gas at atmospheric pressure, the Laplace pressure deficiency in the liquid may exceed one atmosphere if the capillary or pore, is sufficiently small. For water with $\gamma = 72 \text{mNm}^{-1}$ (and assuming zero contact angle) this will happen in pores of about $1.4 \mu\text{m}$ radius and smaller, and the liquid will now exist under a negative pressure, or tension.

The van der Waals isotherm of a typical fluid below its critical temperature is sketched in figure 2. The unstable region BC (where the compressibility is negative) separates the liquid curve AB from the vapour curve CD (where the product is approximately constant). The liquid can exist metastably at negative pressure right down to B, where the compressibility becomes infinite and the liquid 'bursts'.

For common liquids well below the critical temperature, the negative pressure at B is of the order of a hundred atmospheres or more.

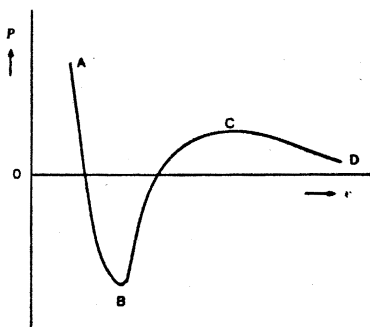


Fig 2

Thus, in the absence of nucleation centres, liquids can withstand quite large tensile stresses or 'negative pressures'.

Attempts to measure the limiting tensile strengths of liquids⁽¹⁾ have encountered difficulties, largely because of the problems of excluding nuclei, such as dust particles, on which vapour bubbles may well form well before the tensile limit is reached. It appears however that when the liquid is confined in small pores, the pore space may be too small to permit the formation of a nucleus of critical size⁽²⁾. Thus, there is no doubt that a capillary-held liquid can exist under quite substantial negative pressures.

This has several practical consequences. The tensile force in the liquid is transmitted to the pore walls and thus the porous solid will behave as though under compression. Indeed, it is well-known that even quite porous solids, such as carbon and porous glasses, shrink when desorption of capillary condensate begins. A more commonplace example is the way in which the bristles of a wetted paint-brush cling together when the first liquid is removed from between them. Some porous media undergo irreversible structural changes on drying, partly attributable to inelastic deformation under this capillary stress.

This is the obverse of the effect seen in mercury intrusion porosimetry, where the liquid is under a positive excess pressure because the interfacial curvature is in the opposite sense. Again, the solid distorts to accommodate the imposed stress.

A further consequence is that in extremely fine-pored solids, the negative pressure in a capillary-condensed liquid may exceed the liquid's true tensile strength, thus imposing a lower limit on the pore size in which capillary condensation can occur. This possibility was foreseen several years ago by Schofield⁽³⁾, and has more recently been shown to be consistent with experimental results^(4,5).

In summary, the pressure deficiency in a capillary-held liquid, which arises from negative interfacial curvature, may exceed the liquid's vapour pressure if the pore size is smaller than 1-2 μm . The liquid is then subjected to a negative

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pressure, which it can withstand metastably provided that bubble nucleation does not occur. The negative pressure may reach 100 atmospheres or more before the limit of metastability is exceeded.

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