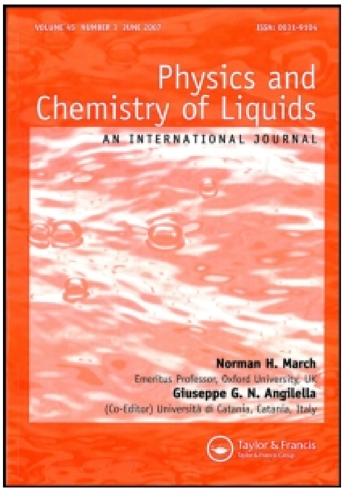

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GRADIENT EXPANSIONS AND BEYOND FOR STRESS TENSOR AND TANGENTIAL PRESSURE DEFICIT THROUGH A PLANAR LIQUID-VAPOUR INTERFACE

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After a discussion of gradient expansions for physical quantities through a planar liquid-vapour interface, two proposals are made as to possible generalizations of the tangential pressure deficit through the interface. One expresses the deficit in terms of force-force correlation functions and the other in terms of the direct correlation function in the presence of the interface. Finally, a very practical approach generalizes Fowler's formula for the surface tension, to obtain an explicit, though now evidently approximate expression for the tangential pressure deficit in the limit when the thickness of the interface tends to zero.

Keywords: Liquid-vapour interface; direct correlation function

PACs Number: 68.10.Cr

I. INTRODUCTION

Considerable interest continues to be shown in the statistical mechanics of inhomogeneous fluids. One of the simplest examples, which is the main focus of the present study, is the planar liquid-vapour interface, taken here to lie in the (xy) place.

It is well known that the corresponding surface tension σ can be written as an integral of the tangential pressure deficit $p - p_t(z)$, where

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$p_t(z)$ is the variation of the tangential pressure induced by the interface, while p is the (constant) normal pressure. Going back to the pioneering work of Kirkwood and Buff [1], based on a pair potential assumption, $p - p_t(z)$ has the explicit form

$$p - p_t(z) = \frac{1}{2} \int d\vec{R}\phi'(R) n_2(z, \vec{R}) \frac{X^2 - Z^2}{R} \tag{1}$$

where the components of $\vec{R}$ have been written as (X, Y, Z) and $\phi'(R) = d\phi/dR$. Here $\phi(\vec{R})$ is the pair potential, and n_2 the pair correlation function in the presence of the inhomogeneity.

Our object in the present study is to seek a generalization of Eq. (1) which avoids the pair potential assumption. Then as is clear from numerous statistical mechanics studies [2–4], the correct tool to use is the direct correlation function $c(\vec{r}, \vec{r}')$. In terms $c(\vec{r}, \vec{r}')$, the integral of the tangential pressure deficit is known from the work of Triezenberg and Zwanzig [2], which they attribute as going back to Yvon. This formula for the surface tension σ reads:

$$\sigma = k_B T \int_{-\infty}^{+\infty} dz \int_{-\infty}^{+\infty} dz' \left[\frac{\partial \varrho(z)}{\partial z} \right] K_2(z, z') \left[\frac{\partial \varrho(z')}{\partial z'} \right] \tag{2}$$

where $\varrho(z)$ is the density profile through the interface and $K_2(z, z')$ is defined precisely in terms of $c(\vec{r}, \vec{r}')$ in Eq. (11) below. The question to which we propose an answer below is 'What is the tangential pressure deficit corresponding to the direct correlation function theory of surface tension summarized in Eq. (2)?' We shall approach this by setting out in Section II a summary of results which employ a low-order gradient expansion in the density profile $\varrho(z)$. Here, precise results are readily written down for the tangential pressure deficit $p - p_t(z)$. They are now posed, however, because of the gradient expansion approximation, in terms of $\varrho(z)$ and its derivatives, and the bulk direct correlation function $c(r, \rho_0)$ where ρ_0 is the (now constant) bulk liquid density. We note here that, recently, March and Tosi [5] have proposed an (inevitably approximate) formula for the direct correlation function $c(\vec{r}, \vec{r}')$ in terms of (a) the bulk direct correlation function $c(r, \rho_0)$, (b) the density profile $\varrho(z)$ and its gradient and (c) the thickness, L say, for the liquid–vapour interface. We shall relate this work to both the gradient expansion treatment of Section II below, as well as to the (formally) exact theory in terms of $c(\vec{r},\vec{r}')$ set out in Section III, while Section IV constitutes a summary, together with some proposals for possible future work in this area.

II. GRADIENT EXPANSION APPROXIMATION FOR TANGENTIAL PRESSURE DEFICIT

Following the study of Yang, Fleming and Gibbs [6], the work of Bhatia and March [7] was concerned with the way such gradient expansions using the variation of the density profile $\varrho(z)$ could lead to the correlation between surface tension ϱ and a bulk property of the dense liquid, the isothermal compressibility κ_T, *via* the 'surface thickness' L: namely

$$\sigma\kappa_T = L \tag{3}$$

This correlation, known for instance to Cahn and Hilliard [8] and to Egelstaff and Widom [9], has been shown recently to apply to monoatomic liquids (*e.g.*, Ar and liquid metallic Na) but also to a wide variety of organic liquids [10].

In deriving Eq. (3) from a gradient expansion approximation, Bhatia and March wrote the (constant) normal pressure through the interface in the form

$$p = \mu\varrho(z) - \psi[\varrho(z)] + \frac{1}{2}A[\varrho(z)]\varrho'(z)^2 \tag{4}$$

where μ is the chemical potential, while $\psi(\rho_0)$ is the local free energy density of a uniform fluid of density ρ_0 and $A(\rho_0)$ is defined in terms of the bulk fluid direct correlation function $c(r,\rho_0)$ by [6]

$$A(\rho_0) = \frac{k_BT}{6}\int r^2c(r,\rho_0)d\vec{r}. \tag{5}$$

The tangential pressure deficit $p - p_t(z)$ is readily written from the surface tension result, going back essentially to van der Waals (see also Ref. [7]):

$$\sigma = \int_{-\infty}^{+\infty} A[\varrho(z)]\varrho'(z)^2dz. \tag{6}$$

This can be shown (see also Ref. [6]) to yield the tangential pressure deficit, quite precisely to the order displayed in the gradient expansion, as

$$p - p_t(z) = A[\varrho(z)]\varrho'(z)^2. \tag{7}$$

If one wishes, the combination Eqs. (7) and (4) can be utilized to write $p_t(z)$ in gradient expansion as

$$p_t(z) = \mu\varrho(z) - \psi[\varrho(z)] - \frac{1}{2}A[\varrho(z)]\varrho'(z)^2. \tag{8}$$

The two formulas (7) and (8) are the main results of the present section, and provide our motivation for seeking a formally exact result for the tangential pressure deficit $p - p_t(z)$, thereby generalizing the low-order result (7).

We note that the result of Eq. (7) can also be written in terms of the stress tensor (first obtained by Lovett in his thesis, see [6]). To lowest order in the gradient expansion the stress tensor is given by

$$\overleftrightarrow{\sigma} = (\mu\varrho - \psi(\varrho))\overleftrightarrow{1} + A(\varrho)\left\{\nabla\varrho\nabla\varrho - \frac{1}{2}(\nabla\varrho)^2\overleftrightarrow{1}\right\} \tag{9}$$

Since the normal ($p_n(z) = p$) and tangential ($p_t(z)$) pressure are given by the diagonal elements σ^{zz} and σ^{xx} respectively, we obtain from $\sigma^{zz} - \sigma^{xx}(z)$ immediately Eq. (7).

III. FORMALLY EXACT PROPOSAL FOR TANGENTIAL PRESSURE DEFICIT

A. The Direct Correlation Function

The results reported in Section II are complete, and quite explicit, for $p - p_t(z)$ to lowest order in the gradient expansion. However, they have motivated us to seek a (formally) exact expression for $p - p_t(z)$ in terms of $\varrho(z)$ appearing already, with its derivative $\partial\varrho/\partial z$, in Eq. (7). One wishes to embody also, in place of $A[\varrho(z)]$ in Eq. (7), defined through Eq. (5) in terms of the bulk direct correlation function, the 'inhomogeneous' direct correlation function $c(\vec{r}, \vec{r}\,')$.

The natural starting point is then the surface tension formula (see [2]):

$$\sigma = k_BT \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dz\,dz' \left[\frac{\partial \varrho(z)}{\partial z}\right] K_2(z,z') \left[\frac{\partial \varrho(z')}{\partial z'}\right] \tag{10}$$

where K_2 is related to $c(\vec{r}, \vec{r}\,')$ by [2]

$$K_2(z,z') = \frac{1}{4}\int d\vec{u}\, u^2 c(0,z;\vec{u},z') \tag{11}$$

where $\vec{u}$ denotes a vector in the (x,y) plane.

If, as March and Tosi note [5] (see also Ref. [11]), $c(\vec{r},\vec{r}\,')$ is approximated by a δ-function form, then the van der Waals-like formula for σ is regained.

Thus, our proposal from the arguments of Section II plus Eq. (10) is that

$$p - p_t(z) = k_BT \frac{\partial \varrho(z)}{\partial z} \int_{-\infty}^{+\infty} dz' K_2(z,z') \frac{\partial \varrho(z')}{\partial z'} \tag{12}$$

In principle, one could add a quantity, $\Delta(z)$ say, to the RHS of Eq. (12) provided that

$$\int_{-\infty}^{+\infty} dz\, \Delta(z) = 0 \tag{13}$$

However, the close connection of Eq. (12) with the precise gradient result (7) provides a strong argument, though not a final proof, that Eq. (12) is a complete, and formally exact, expression for the tangential pressure deficit. (In Appendix A we give an expression for $p - p_t(z)$ in the case of pair potentials).

B. Force-Force Correlation Function

An equally valid form for the pressure deficit follows from the force-force correlation function as shown by Schofield [3]. An explicit form of the stress tensor for an (assumed) pair potential $\phi(r)$ is given by

$$\sigma^{\alpha\beta}(\vec{r}) = \sum_i (p_i^\alpha p_i^\beta/m)\delta(\vec{r} - \vec{r}_i)$$
$$-\frac{1}{2}\int d\vec{R}\frac{R^\alpha R^\beta}{R}\frac{\partial \phi(R)}{\partial R}\int_0^1 d\lambda\, n(\vec{r} - \lambda\vec{R}, \vec{r} + (1-\lambda)\vec{R}) \tag{14}$$

with $n(\vec{r},\vec{r}\,')$ the pair density and the sum is taken over all particles.

The mean value $\langle\sigma^{\alpha\beta}(\vec{R})\rangle$ must be a function of Z only in the present case of a liquid–vapour interface in the (x, y) plane.

The component $\langle\sigma^{zz}(\vec{R})\rangle$ of the mean value of the stress tensor must be a constant through the interface, and represents the pressure. This, at least formally, transcends then the low-order gradient expansion result for the pressure in Eq. (4), though that equation, being characterized by the density profile $\varrho(z)$ and the (bulk) direct correlation function has already escaped from the mould of pair potential theories.

Let us form what is, in essence, the tangential pressure deficit $p-p_t(z)$ from Eq. (14), namely

$$p-p_t(z)=\langle\sigma^{zz}(\vec{r})\rangle-\langle\sigma^{xx}(\vec{r})\rangle \tag{15}$$

The first term on the RHS of Eq. (14), when averaged, involves the thermal energy k_BT times the density profile $\varrho(z)$ and makes no contribution to the tangential pressure deficit. Hence we can write

$$p-p_t(z)=\frac{1}{2}\left\langle\int d\vec{R}\left(X\frac{\partial\phi}{\partial X}-Z\frac{\partial\phi}{\partial Z}\right)\int_0^1 d\lambda\, n(\vec{r}-\lambda\vec{R},\vec{r}+(1-\lambda)\vec{R})\right\rangle \tag{16}$$

On integrating this Eq. (16) over all z, this must lead to Schofield's equation (5) which reads

$$\begin{aligned}\sigma&=\int_{-\infty}^{+\infty}[p-p_t(z)]dz\\&=\frac{1}{2}\int_{-\infty}^{+\infty}dz\int d\vec{R}\,n_2(\vec{r},\vec{r}+\vec{R})\left[X\frac{\partial\phi}{\partial X}-Z\frac{\partial\phi}{\partial Z}\right]\end{aligned} \tag{17}$$

Returning to Eq. (16), we choose therefore to write, following the pioneering work of Kirkwood and Buff [1]:

$$p-p_t(z)=\frac{1}{2}\int d\vec{R}\,n_2(\vec{r},\vec{r}+\vec{R})\left[X\frac{\partial\phi}{\partial X}-Z\frac{\partial\phi}{\partial Z}\right] \tag{18}$$

$$=\frac{1}{2}\int d\vec{R}\,n_2(\vec{r},\vec{r}+\vec{R})\left[X^2\frac{\partial^2\phi}{\partial Z^2}-Z^2\frac{\partial^2\phi}{\partial X^2}\right] \tag{19}$$

where the second line follows from the fact that $\phi(R)$ is spherical symmetric.

With $J^{\alpha}(\vec{R})$ defined as in Schofield's work as the momentum density through

$$J^{\alpha}(\vec{r}) = \sum_{i} p_i^{\alpha}\delta(\vec{r} - \vec{r}_i) \tag{20}$$

Schofield proves the result:

$$k_B T\left\langle J^{\alpha}(\vec{r})\ddot{J}^{\beta}(\vec{r}\,')\right\rangle = k_B T n_2(\vec{r},\vec{r}\,')\nabla_{\alpha}\nabla_{\beta}\phi(|\vec{r} - \vec{r}\,'|) + L(\vec{r},\vec{r}\,') \tag{21}$$

where $L(\vec{r},\vec{r}\,')$ represents explicitly what Schofield calls "local" terms.

Hence Eq. (19) can be rewritten in the form, using

$$\left\langle J^{\alpha}(\vec{r})\ddot{J}^{\beta}(\vec{r}\,')\right\rangle = -\left\langle \dot{J}^{\alpha}(\vec{r})\dot{J}^{\beta}(\vec{r}\,')\right\rangle \tag{22}$$

$$p - p_t(z) = \frac{1}{2k_B T}\int d\vec{R}\left[X^2\left\langle \dot{J}^{z}(\vec{r})\dot{J}^{z}(\vec{r} + \vec{R})\right\rangle - Z^2\left\langle \dot{J}^{x}(\vec{r})\dot{J}^{x}(\vec{r} + \vec{R})\right\rangle\right] \tag{23}$$

Having already assumed in Eq. (21) that the "local" contribution only involves, as Schofield asserts, $\delta(\vec{r} - \vec{r}\,')$ and its first and second derivatives, the function $L(\vec{r},\vec{r}\,')$ makes no contribution to Eq. (23) because of the factors X^2 and Z^2.

Thus, the conclusion of this section is that the tangential pressure deficit is related to appropriate spatial moments of force–force correlation functions. Integrating Eq. (23) over z from $-\infty$ to $+\infty$ immediately gives back Schofield's equation (18) for $k_B T$ times the surface tension.

In Appendix B we have added some comments on curved interfaces.

IV. SUMMARY AND POSSIBLE FUTURE DIRECTIONS

The main aim of the present paper has been to establish first the tangential pressure deficit and the closely related stress tensor [6] in the lowest-order gradient expansion theory.

We have then transcended this low-order gradient approximation and have then been led, in terms of the direct correlation function $c(\vec{r},\vec{r}')$ in the presence of the planar liquid–vapour interface to the proposal (12) in terms of the density profile $\varrho(z)$ and $c(\vec{r},\vec{r}')$ through Eq. (11). We have also established an expression of the tangential pressure deficit in terms of the force–force correlation function. We note however, that, in principle, both (12) and (23) could be modified by the addition of a function $\Delta(z)$, which then must satisfy the sum rule (13). To lowest order in the gradient expansion, we have proved however that $\Delta(z) = 0$ and it is a matter for future studies to prove that $\Delta(z)$ is zero to all orders.

It would, of course, be very important if it proved possible by suitable experimental techniques to measure directly the tangential pressure $p_t(z)$ (for example by neutron scattering studies of correlation functions). Also, it seems to us that the way in which $p_t(z)$ tends to the (normal) pressure p as $|z| \to \infty$ is a matter of some theoretical interest, and should be amenable to attack using hydrodynamic equations.

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APPENDIX A

A very early attempt to construct a pair potential theory of surface tension σ at a planar liquid–vapour interface goes back to Fowler [12]. Though Fowler's derivation was different, one can obtain his result from Eq. (1) by making two approximations. The first is to write

$n_2(\vec{r}, \vec{r} + \vec{R})$ in terms of $\varrho(z)$ and the bulk pair correlation function $g(R)$ in the dense liquid phase [13], [14]

$$n_2(\vec{r}, \vec{r} + \vec{R}) \approx \varrho(z)\varrho(z + Z)g(R) \tag{A1}$$

Inserting this into Eq. (1), the further approximation of Fowler is then to take a step model of the density profile, namely

$$\begin{aligned} \varrho(z) &= 0 \quad 0 < z < \infty \\ &= \varrho_l \quad -\infty < z < 0 \end{aligned} \tag{A2}$$

Inserting these two approximations (A1) and (A2) into the initially exact pair potential result for the tangential pressure deficit, Eq. (1) yields then

$$p - p_t(z) = -\frac{\pi}{2}\varrho_l^2\theta(-z)\int_0^\infty dR\phi'(R)g(R)\left(R^2 z - z^3\right)\theta(R - z)\theta(R + z) \tag{A3}$$

where $\theta(z)$ is the Heaviside function, which expresses the fact that the tangential pressure deficit is zero for the vapour phase ($z > 0$) within the Fowler step model. Integrating Eq. (A3) over z immediately yields Fowler's expression for the surface tension [12]:

$$\sigma = \frac{\pi}{8}\varrho_l^2 \int_0^\infty dR\, R^4 \phi'(R) g(R) \tag{A4}$$

APPENDIX B SOME COMMENTS ON CURVED INTERFACES

As discussed by Yang *et al.* [6] Lovett's formula for the stress tensor, quoted in Section II for the planar interface is in fact true also for curved interfaces, of course at the level of the lowest-order gradient expansion theory.

Transcending the gradient expansion, the analogue of the Triezenberg-Zwanzig theory for curved interfaces has been set out by Henderson and Schofield [4]. They derived an expression for the surface tension of a spherical interface, of radius R_e, which is valid within the leading-order difference from the planar interface. In analogy with expression (12), we therefore define a *differential surface tension* as

$$D_\sigma(r) = \frac{\pi}{2} k_B T \varrho'(r) \int_0^\infty dr' \varrho'(r') \int_{|\vec{r}-\vec{r}'|}^\infty dR\, R^2 [R^2 - (r - r')^2] c(R, r, r') + O((d/R_e)^2) \tag{B1}$$

where d is a measure of the range of the direct correlation function $c(R, r, r')$ and $R = |\vec{r} - \vec{r}'|$. Integration of expression (B1) over r gives back the formula for the surface tension of Henderson and Schofield. Of course one can add a term, $\Delta(r)$ say, to Eq. (B1) which integrates to 0: $\int_0^{+\infty} \Delta(r) dr = 0$. We can readily prove that $D_\sigma(r)$ in the limit of the lowest order gradient expansion reduces to

$$D_\sigma(r) \to A[\varrho(r)] \left(\frac{\partial \varrho(r)}{\partial r} \right)^2 \tag{B2}$$

with $A[\varrho(r)]$ given by Eq. (5). However, without explicit knowledge of the R_e-dependence of $D_\sigma(r)$ beyond the formal statement in Eq. (B1) we are not presently able to show the relation between expression (B1) and expression (12), due to the difference in spherical coordinates and the planar limit of the interface in Eq. (12).