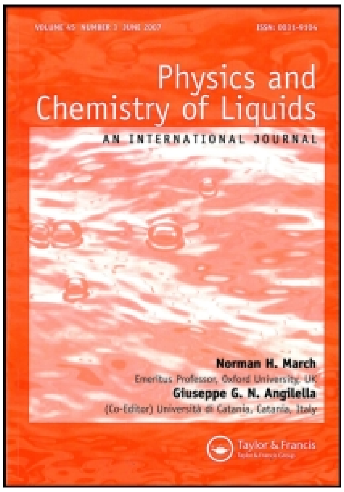

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Statistical Mechanical Theory of Liquid Surface Tension

A. B. Bhatia[a,b]; N. H. March[a]
[a] Theoretical Chemistry Department, University of Oxford, Oxford [b] Physics Department, University of Alberta Edmonton Canada Work supported in part by the National Research Council, Canada

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Review Article

Statistical Mechanical Theory of Liquid Surface Tension

A. B. BHATIA† and N. H. MARCH,

Theoretical Chemistry Department, University of Oxford,
1 South Parks Road, Oxford. OX1 3TG

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Two statistical mechanical methods of calculating liquid surface tension are considered. The first is via the virial theorem and the second is based on a variational principle for the free energy. The connection with existing theories is discussed.

1 INTRODUCTION

There is currently considerable interest in the theories of surface tension σ at the liquid-vapour interface.[1] When the atoms interact via a pair potential, σ can be expressed in terms of the pair potential ϕ and the pair distribution function by the Kirkwood–Buff formula.[2] An alternative formula, derived by Triezenberg and Zwanzig (TZ) using a fluctuation approach[3] and attributed by them originally to Yvon, expresses σ in terms of the density gradient dn/dz and the direct correlation function $C^{(2)}(\mathbf{r}_1\mathbf{r}_2)$ for the inhomogeneous system which has a planar surface perpendicular to the z axis. An alternative derivation of TZ formula has been given by Lovett *et al.*,[4] their approach though formally different is not physically dissimilar to that of TZ.

In this article, intended as a review, we first apply the virial theorem to a classical liquid with pairwise interatomic potential to show that it leads in a simple manner to a formula for σ which is equivalent to the Kirkwood–Buff result.

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In the next section we give a formalism using a variational principle on the free energy A (regarded as a functional of $n(\mathbf{r})$) and obtain a formula for σ by expressing A in the form of the thermodynamic identity

$$A = \mu N - PV + \sigma a \tag{1.1}$$

where a is the area of the plane interface.

The formula thus developed can be used to evaluate σ if the functional form of A is known. One can also show that this expression for σ can be expressed as a series involving the various order direct correlation functions of a homogeneous system. Although we have not been able to sum the series and show its equivalence (or otherwise) to the TZ formula, it is felt that formalism presented here is of interest since it is not based on the fluctuation approach. For the case where the free energy density is gradient expanded to second order in dn/dz, our formula leads to that derived by Yang *et al.*[5]

2 VIRIAL FORMULA WITH PAIR POTENTIALS

For an inhomogeneous system, with the density n being a function of z only, the stress tensor has the symmetry $\Pi_{xx} = \Pi_{yy}$; $\Pi_{zz} = -P$, the pressure and $\Pi_{xy} = \Pi_{xz} = \Pi_{yz} = 0$. P is a constant independent of z.

The contribution to the virial from the stress tensor is

$$\begin{aligned}\int [\Pi_{xx}(z) + \Pi_{yy}(z) + \Pi_{zz}]\,\mathrm{d}\mathbf{r} &= a\int(\Pi_{xx}(z) + P)\,\mathrm{d}z + a\int(\Pi_{yy}(z) + P)\,\mathrm{d}z - a\int 3P\,\mathrm{d}z\\ &= 2\sigma a - 3PV\end{aligned} \tag{2.1}$$

where a is the area perpendicular to z, and where we have used the "mechanical" definition of surface tension (for a planar surface)

$$\sigma = \int(\Pi_{xx} + P)\,\mathrm{d}z = \int(\Pi_{yy} + P)\,\mathrm{d}z \tag{2.2}$$

Adding to Eq. (2.1) the contribution to the virial from the interatomic pair potential ϕ and equating the sum to $-3Nk_BT$ one finds

$$-3Nk_BT = 2\sigma a - 3PV - \frac{a}{2}\int \rho\phi'(\rho)n^{(2)}(\rho, z)\,\mathrm{d}^3\rho\,\mathrm{d}z \tag{2.3}$$

where $\boldsymbol{\rho}$ is the vector separation between two particles and $\phi'(\rho) \equiv \mathrm{d}\phi/\mathrm{d}\rho$. Noting the identity

$$PV - Nk_BT \equiv a\int P\,\mathrm{d}z - k_BTa\int n(z)\,\mathrm{d}z \tag{2.4}$$

Eq. (2.3) gives for σ the expression in terms of the pair function $n^{(2)}$

$$\sigma = \frac{3}{2}\int\left[P - n(z)k_BT + \frac{1}{6}\int n^{(2)}(\rho, z)\rho\phi'(\rho)\,\mathrm{d}^3\rho\right]\mathrm{d}z \tag{2.5}$$

Though the above derivation of Eq. (2.5) appears to be new, one can establish its equivalence to the well known Kirkwood–Buff formula as follows. One invokes the known result that

$$P \equiv -\Pi_{zz} = k_BTn(z) - \frac{1}{2}\int n^{(2)}(\boldsymbol{\rho}, z)\frac{\zeta^2}{\rho}\phi'(\rho)\,\mathrm{d}^3\rho \tag{2.6}$$

where $\boldsymbol{\rho}$ has components ξ, η, ζ. Substituting (2.6) in (2.5) and utilising the symmetry between ξ and η yields

$$\sigma = \frac{1}{2}\int n^{(2)}(\boldsymbol{\rho}, z)\frac{\xi^2 - \zeta^2}{\rho}\phi'(\rho)\,\mathrm{d}^3\rho\,\mathrm{d}z \tag{2.7}$$

which is the Kirkwood–Buff result.

One can, of course, rederive σ in the form of Eq. (2.7) or that of (2.5) from (2.2) and (2.6), using the expression[6] for $\Pi_{xx}(z)$

$$\Pi_{xx}(z) = -k_BTn(z) + \frac{1}{2}\int n^{(2)}(\boldsymbol{\rho}, z)\frac{\xi^2}{\rho}\phi'(\rho)\,\mathrm{d}^3\rho, \tag{2.8}$$

the expressions Π_{yy} and Π_{zz} following from (2.8) by replacing ξ^2 by η^2 and ζ^2 respectively.

3 SURFACE TENSION FROM VARIATIONAL PRINCIPLE FOR FREE ENERGY

Following Yang *et al.*,[5] let F' be related to A by

$$F' = \beta A - \beta\int \mathrm{d}^3rU(\mathbf{r})n(\mathbf{r}) \tag{3.1}$$

where $\beta = 1/k_B T$ and $U(\mathbf{r})$ is the external potential. F' and A are regarded as functionals of $n(\mathbf{r})$ and we have from Yang *et al.*,

$$\frac{\delta F'}{\delta n(\mathbf{r})} = \beta\mu - \beta U(\mathbf{r}) \tag{3.2}$$

$$= \ln(n(r)) + (\ln \Lambda^3) - C(\mathbf{r});\ \Lambda = \left(\frac{\beta h^2}{2\pi M}\right)^{1/2}. \tag{3.3}$$

Here μ is the chemical potential while Eq. (3.3) defines $C(r)$. Its functional derivatives are the various order direct correlation functions: thus

$$C^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta C(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} = \frac{\delta C(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)}$$

$$C^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) = \frac{\delta C^{(2)}(\mathbf{r}_1\mathbf{r}_2)}{\delta n(\mathbf{r}_3)} \qquad \text{etc.} \tag{3.4}$$

If we write F' as

$$F' = F'_0 - \Phi[n(r)] \tag{3.5}$$

where

$$F'_0 = \int d^3r\, n(\mathbf{r})\{(\ln(n(\mathbf{r}))\Lambda^3) - 1\}, \tag{3.6}$$

then Φ is a functional of $n(\mathbf{r})$ and

$$\frac{\delta \Phi}{\delta n(\mathbf{r})} = C(r),\ \frac{\delta^2 \Phi}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)} = C^{(2)}(\mathbf{r}_1\mathbf{r}_2) \qquad \text{etc.} \tag{3.7}$$

It will be convenient in the following also to write F' in the absence of the external potential as

$$F' = \beta A = \beta \int \psi(n(\mathbf{r}))\, d^3r - \phi[n(\mathbf{r})] \tag{3.8}$$

where $\psi(n(\mathbf{r}))$ is a function of the local density $n(\mathbf{r})$ and $\phi[n(r)]$ is a functional of $n(r)$ such that if dn/dx, dn/dy, dn/dz are all identically zero, $\phi \equiv 0$.

3.1 Density profile

Taking the gradient of Eq. (3.2)

$$-\beta\nabla U(\mathbf{r}) = \nabla \frac{\delta F'}{\delta n(\mathbf{r})} = \frac{1}{n(\mathbf{r})}\nabla n(\mathbf{r}) - \nabla C(\mathbf{r})$$

From the property that $C(\mathbf{r})$ is a functional of $n(\mathbf{r})$ it follows that

$$\nabla C(\mathbf{r}) = \int C^{(2)}(\mathbf{r}\mathbf{r}')\nabla n(\mathbf{r}')\,\mathrm{d}^3r'$$

and hence

$$-\beta\nabla U(\mathbf{r}) = \frac{1}{n(\mathbf{r})}\nabla n(\mathbf{r}) - \int C^{(2)}(\mathbf{r}\mathbf{r}')\nabla n(\mathbf{r}')\,\mathrm{d}^3r' \tag{3.9}$$

which is the equation for the density profile given by Lovett, Mou and Buff.[7] In the absence of the external potential ($\nabla U(r) = 0$) (3.9) reduces to the equation of TZ. We observe that when $U = 0$, $F' = \beta A$, the equation for equilibrium is from (3.2)

$$\frac{\delta A}{\delta n(\mathbf{r})} = \mu$$

which is the Euler equation for the problem.

3.2 Formula for surface tension

We know from thermodynamics that in the presence of a planar surface (which we shall take as in section 2 perpendicular to the z-axis), A has the form (1.1).

This expression leads to a formula for σ in terms of the quantity ϕ introduced in Eq. (3.8).

Setting $U(\mathbf{r}) = 0$, Eqs. (3.2) and (3.8) give

$$\beta\mu = \beta\frac{\mathrm{d}\psi(n(r))}{\mathrm{d}n} - \frac{\delta\phi}{\delta n(\mathbf{r})}$$

Multiplying this equation by $\mathrm{d}n/\mathrm{d}z$ we have

$$\beta\frac{\mathrm{d}}{\mathrm{d}z}\{\psi(n) - \mu n(z)\} = \frac{\mathrm{d}n}{\mathrm{d}z}\frac{\delta\phi}{\delta n(\mathbf{r})}$$

and introducing

$$\frac{\mathrm{d}n}{\mathrm{d}z}\frac{\delta\phi}{\delta n(\mathbf{r})} \equiv \frac{\mathrm{d}G}{\mathrm{d}z} \tag{3.10}$$

one has

$$\frac{\mathrm{d}}{\mathrm{d}z}\left\{\mu n(z) - \psi(n) + \frac{1}{\beta}G\right\} = 0 \tag{3.11}$$

Now when $\phi \equiv 0$, $G = 0$, the term within brackets { } $\mu n - \psi$ is just the pressure for a homogeneous system. Hence we can identify

$$P = \mu n(z) - \psi(n) + \frac{1}{\beta} G \tag{3.12}$$

Integrating over all the volume, using (3.8) to eliminate $\psi(n)$ and remembering that $F' = \beta A$, we have

$$PV = \mu N - A + \frac{1}{\beta}\left\{\int G \, \mathrm{d}^3 r - \phi\right\} \tag{3.13}$$

Comparing with (1.1), one obtains

$$\sigma = \frac{k_B T}{a}\left\{\int G \, \mathrm{d}^3 r - \phi\right\} \tag{3.14}$$

which is the formula we wished to derive. If ϕ is a known functional of $n(\mathbf{r})$, σ is calculable from (3.14).

First we observe that if ϕ were of the local form

$$\phi = \int \mathscr{F}(n(\mathbf{r})) \, \mathrm{d}\mathbf{r} \tag{3.15}$$

where $\mathscr{F}$ is an arbitrary function (not functional) of $n(\mathbf{r})$ then

$$\frac{\delta \phi}{\delta n(\mathbf{r})} = \mathscr{F}'(n), \; \mathscr{F}' = \frac{\mathrm{d}\mathscr{F}}{\mathrm{d}n} \tag{3.16}$$

$$\frac{\mathrm{d}G}{\mathrm{d}z} = \frac{\mathrm{d}n}{\mathrm{d}z} \mathscr{F}'(n) = \frac{\mathrm{d}}{\mathrm{d}z} \mathscr{F}(n) \tag{3.17}$$

or $G = \mathscr{F}$, since when $\mathscr{F} \equiv 0$, $G = 0$ by definition. Hence $\sigma = 0$. Therefore we can add a local part to ϕ without affecting the value of σ.

In particular, we can replace ϕ by Φ of Eq. (3.5) and write σ in the form

$$\sigma = \frac{k_B T}{a}\left\{\int \tilde{G} \, \mathrm{d}^3 r - \Phi\right\} \tag{3.18}$$

where $\tilde{G}$ is such that

$$\frac{\mathrm{d}\tilde{G}}{\mathrm{d}z} = \frac{\mathrm{d}n}{\mathrm{d}z} \frac{\delta \Phi}{\delta n(\mathbf{r})} = \frac{\mathrm{d}n}{\mathrm{d}z} C(\mathbf{r}) \tag{3.19}$$

RELATION TO TRIEZENBERG–ZWANZIG FORMULA

The original objective in deriving (3.18) was to make contact with the TZ formula for the surface tension, based on expressing the total free energy in the form (1.1). This seemed desirable, since the TZ derivation starts with changes in A due to fluctuations in $n(z)$ from the equilibrium profile. If we make a Taylor (functional derivative) expansion of Φ, $\tilde{G}$ in (3.18), we see that σ can be expressed as a series involving increasingly high order of direct correlation functions of a homogeneous system. However, we have not been able to sum the series to obtain a closed form for σ and thus show the equivalence (or otherwise) of (3.18) to the T-Z formula.

DENSITY GRADIENT EXPANSION

First we observe that if we write the Helmholtz free energy

$$A = \int \psi(r)\,\mathrm{d}^3r = \int \psi(n(r))\,\mathrm{d}^3r + \int \psi_{nl}(r)\,\mathrm{d}^3r \tag{3.20}$$

where ψ_{nl} is the non-local part of $\psi(r)$, then $\phi[n(r)]$ of Eq. (3.8):

$$\phi[n(r)] = -\beta \int \psi_{nl}(\mathbf{r})\,\mathrm{d}^3r. \tag{3.21}$$

If ψ_{nl} is a function of $n(z)$ and its first derivative only, then a simple expression for σ can be obtained in terms of ψ_{nl}. We have

$$\frac{\delta\phi[n(r)]}{\delta n(r)} = -\beta\left[\frac{\partial\psi_{nl}}{\partial n} - \frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial\psi_{nl}}{\partial n_z}\right] \tag{3.22}$$

where $n_z \equiv \mathrm{d}n/\mathrm{d}z$. Hence

$$\begin{aligned}\frac{\mathrm{d}G}{\mathrm{d}z} &= \frac{\mathrm{d}n}{\mathrm{d}z}\frac{\delta\phi[n(\mathbf{r})]}{\delta n(\mathbf{r})} \\ &= -\beta\frac{\mathrm{d}}{\mathrm{d}z}\left(\psi_{nl} - n_z\frac{\partial\psi_{nl}}{\partial n_z}\right)\end{aligned} \tag{3.23}$$

where we have used the fact that

$$\frac{\mathrm{d}}{\mathrm{d}z}\psi_{nl} = \frac{\partial\psi_{nl}}{\partial n}\frac{\mathrm{d}n}{\mathrm{d}z} + \frac{\partial\psi_{nl}}{\partial n_z}\frac{\mathrm{d}n_z}{\mathrm{d}z}$$

Now when $\psi_{nl} \equiv 0$, $G = 0$, hence

$$G = -\beta\left(\psi_{nl} - n_z\frac{\partial\psi_{nl}}{\partial n_z}\right) \tag{3.24}$$

Substituting (3.21) and (3.24) in (3.14) and noting that ψ_{nl} is independent of x and y coordinates, one gets

$$\sigma = \int n_z \frac{\partial \psi_{nl}}{\partial n_z} \, \mathrm{d}z \tag{3.25}$$

Yang *et al.*, have shown that to second order in $\mathrm{d}n/\mathrm{d}z$,

$$\psi_{nl} = \tfrac{1}{2}\mathscr{A}(n(z))\left(\frac{\mathrm{d}n}{\mathrm{d}z}\right)^2 \tag{3.26}$$

where

$$\mathscr{A}(n) = \left(\frac{k_B T}{6}\right) \int \mathrm{d}^3 r \, r^2 C^{(2)}(\mathbf{r}n).$$

Substituting (3.26) in (3.25) gives

$$\sigma = \int \left(\frac{\mathrm{d}n}{\mathrm{d}z}\right)^2 \mathscr{A}(n) \, \mathrm{d}z \tag{3.27}$$

which is just the expression for σ of Yang *et al.*,[5] derived there in another manner.

NON-LOCAL PRESSURE AND FREE ENERGY DENSITY FORMULA

An inspection of (3.12) shows that the non-local (P_{nl}) contribution to P in (3.12) is just G/β. Hence remembering (3.21) and that P_{nl} and ψ_{nl} are functions of z only, expression (3.14) for σ becomes

$$\sigma = \int (P_{nl} + \psi_{nl}) \, \mathrm{d}z \tag{3.28}$$

For the case where ψ_{nl} is quadratic in $\mathrm{d}n/\mathrm{d}z$, it is easily seen that $P_{nl} = \psi_{nl}$, so that the two make equal contributions to σ. In general this will not be the case.

Eliminating $P_{nl} \equiv 1/\beta G$, between (3.12) and (3.14) and using (3.21) gives for σ

$$\sigma = \int (P - P_0(z)) \, \mathrm{d}z \tag{3.29}$$

where

$$P_0(z) \equiv \mu n(z) - \psi(n) - \psi_{nl}. \tag{3.30}$$

Comparison of Eq. (3.29) with (2.2) suggests that for this case (of planar symmetry)

$$\Pi_{xx}(z) = \Pi_{yy}(z) = -P_0(z) \tag{3.31}$$

4 SUMMARY

The virial theorem has been used to formulate a pair potential theory of surface tension σ, which has been shown to be equivalent to the Kirkwood–Buff formula.

A new expression for σ, namely (3.14) has been derived variationally. The relation to the TZ formula is discussed, but the equivalence has not been demonstrated as this involves summing a series involving increasingly high order direct correlation functions. The formula (3.14) is readily shown to give back the gradient expansion results of Yang *et al.*[5]

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