Fluctuation Theory of Surface Tension

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We derive a statistical mechanical expression for the surface tension of a liquid-vapor interface. It contains the density profile and the direct correlation function in the vicinity of the interface. When a local Ornstein-Zernike approximation is made on the direct correlation function, the surface-tension theory of Fisk and Widom is obtained.

Recent investigations of surface phenomena near the liquid-vapor critical point by Fisk and Widom,[1] by Felderhof,[2] and by Buff, Lovett, and Stillinger,[3] were based on variants of the classic Van der Waals theory of surface tension. We present here an exact generalization of this theory. In particular, we give a derivation of a formula for surface tension which involves the density profile of a liquid-vapor interface and also the direct correlation function in the vicinity of the interface. When the conventional Ornstein-Zernike approximation is made on the direct correlation function, the results of Fisk and Widom follow directly.

While our derivation is new, and the result has not previously appeared in the published scientific literature, the result is in fact not new.[4] In view of the importance of the result, it seems desirable to give a new and simple derivation.

Consider a fluid in a vertical gravitational field. The magnitude of the field is taken sufficiently weak that its only effect is to produce a liquid-vapor interface. The vertical direction is the z axis of a coordinate system, and $\vec{r}$ denotes a vector in the x,y plane.

The equilibrium density of the fluid is $n_0(z)$. As z becomes large and negative, this density approaches the density $n(l)$ of the uniform liquid phase; and as z becomes large and positive, it approaches the gas density $n(g)$. We use the conventional Gibbs equimolar surface to define the location of the interface, and we select the coordinate origin so that the equilibrium Gibbs surface is the plane $(x,y,0)$.

Now suppose that a density fluctuation occurs. The new density is $n(\vec{r},z)$, and the fluctuation is $n_1(\vec{r},z) = n(\vec{r},z) - n_0(z)$. As the density fluctuates, the location of the Gibbs surface also fluctuates. The instantaneous position of the Gibbs surface is $z_0(r)$, and is given by

$$z_0(\vec{r}) = \int dz\, n_1(\vec{r},z)/\Delta n\,, \tag{1}$$

where $\Delta n = n(l) - n(g)$. The area of the equilibrium surface is A_0, and the area of the new surface is A. These are related by

$$A = A_0 + \tfrac{1}{2}\int d^2r\, |\nabla_r z_0(\vec{r})|^2\,, \tag{2}$$

where the integral is taken over the original surface A_0. Because of translational symmetry in the x,y plane, we may expand all fluctuations in Fourier components,

$$n_1(\vec{r},z) = \textstyle\sum_q n_1(\vec{q},z)\exp(i\vec{q}\cdot\vec{r})\,, \tag{3}$$

where $\vec{q}$ is a vector in the x,y plane. The position of the Gibbs surface has the Fourier expansion

$$z_0(\vec{r}) = \textstyle\sum_q z_0(\vec{q})\exp(i\vec{q}\cdot\vec{r})\,; \tag{4}$$

the coefficients are given by

$$z_0(\vec{q}) = \int dz\, n_1(\vec{q},z)/\Delta n\,. \tag{5}$$

The change in area due to density fluctuations is

$$A - A_0 = \tfrac{1}{2}A_0 \textstyle\sum_q q^2 |z_0(\vec{q})|^2\,. \tag{6}$$

Now let us calculate the change in free energy due to density fluctuations. According to familiar fluctuation theory, the free-energy change is quadratic in the fluctuations,

$$\Delta F = \tfrac{1}{2}kT\int d^2r_1\,dz_1\,d^2r_2\,dz_2\, n_1(\vec{r}_1,z_1)K(\vec{r}_1,z_1;\vec{r}_2,z_2)n_1(\vec{r}_2,z_2)\,, \tag{7}$$

and the inverse of the integral kernel $K(r_1,z_1;r_2,z_2)$ is related to the equilibrium second moments of density fluctuations by

$$K^{-1}(\vec{r}_1,z_1;\vec{r}_2,z_2) = \langle n_1(\vec{r}_1,z_1)n_1(\vec{r}_2,z_2)\rangle\,. \tag{8}$$

According to the statistical mechanical theory of inhomogeneous systems, as discussed, e.g., by Percus,[5] this kernel can be expressed in terms of the density $n_0(z)$ and the direct correlation function $C(r_1,z_1;r_2,z_2)$,

$$K(\vec r_1,z_1;\vec r_2,z_2)=\delta(\vec r_1-\vec r_2)\delta(z_1-z_2)/n_0(z_1)-C(\vec r_1,z_1;\vec r_2,z_2). \tag{9}$$

In Fourier components, the above equations become

$$\Delta F=\tfrac{1}{2}A_0kT\int dz_1\int dz_2\sum\nolimits_q n_1{}^*(\vec q,z_1)\hat K(\vec q;z_1,z_2)n_1(\vec q,z_2), \tag{10}$$

$$\hat K(\vec q;z_1,z_2)=\delta(z_1-z_2)/n_0(z_1)-\hat C(q;z_1,z_2). \tag{11}$$

We use the definition

$$\hat C(\vec q;z_1,z_2)=\int d^2r_2\,C_1(0,z_1;\vec r_2,z_2)\exp(i\vec q\cdot\vec r_2). \tag{12}$$

Because fluctuations corresponding to different values of $\vec q$ are not coupled in the quadratic approximation, we may consider throughout only a single value of $\vec q$.

The idea of the derivation is to focus attention on density fluctuations which change the surface area, to find the changes in free energy and area associated with these fluctuations, and to obtain the surface tension α from the ratio of these changes using the thermodynamic formula

$$\Delta F=\alpha(A-A_0). \tag{13}$$

One approach is to find the density fluctuation which minimizes the free energy under the constraint of a given change in surface area. This approach gives the same results, in the long-wavelength limit, as the following more intuitive argument.

Consider a spontaneous long-wavelength fluctuation in the position $z_0(\vec q)$ of the Gibbs surface. The amplitude of the fluctuation is very small, so that the surface deviates only very slightly from planarity. It is reasonable to suppose that this fluctuation in the surface is associated with a vertical shift in the equilibrium density profile,

$$n_0(z)\rightarrow n_0(z-z_0(\vec q)), \tag{14}$$

without any change in the shape of the profile. Thus the change in density is

$$n_1(\vec q;z)\cong -z_0(\vec q)\,dn_0(z)/dz. \tag{15}$$

When this is substituted in Eq. (10), we get the free-energy change

$$\Delta F=\tfrac{1}{2}A_0kT|z_0(\vec q)|^2\int dz_1\int dz_2[dn_0(z_1)/dz_1]\hat K(\vec q;z_1,z_2)\,dn_0(z_2)/dz_2. \tag{16}$$

Let us expand the kernel $\hat K$ in powers of q;

$$\hat K(\vec q;z_1,z_2)=K_0(z_1,z_2)+q^2K_2(z_1,z_2)+\cdots. \tag{17}$$

In particular, the second-order coefficient is

$$K_2(z_1,z_2)=\tfrac{1}{4}\int dz_1\,dz_2\,d^2r_2\,r_2{}^2C(0,z_1;\vec r_2,z_2). \tag{18}$$

In the limit $q\rightarrow 0$, there is no change at all in the surface area, so that there will be no change in free energy. This indicates that $dn_0(z)/dz$ is an eigenfunction of the kernel $K_0(z_1,z_2)$ with zero eigenvalue, or

$$\int dz_2K_0(z_1,z_2)\,dn_0(z_2)/dz_2=0. \tag{19}$$

If the direct correlation function is known, this can be solved for the equilibrium surface profile. In particular, if we make a local Ornstein-Zernike approximation on $\hat C$, Eq. (19) reduces to the one used by Fisk and Widom to find their approximate surface profile. We return to this point shortly.

The remaining term is quadratic in $\vec q$; on comparing it with the corresponding change in surface area, we find the following expression[6] for the surface tension:

$$\alpha=kT\int dz_1\,dz_2[dn_0(z_1)/dz_1]K_2(z_1,z_2)\,dn_0(z_2)/dz_2. \tag{20}$$

It should be noted that this expression makes no explicit reference to intermolecular potentials. [We have not been able to find any direct connection between Eq. (20) and the well-known formula for α derived by Kirkwood and Buff.[7]]

The relation of our theory to those of Fisk and Widom and Felderhof can be seen easily as follows. Let us make a local Ornstein-Zernike approximation on the direct correlation function,

$$\hat{C}(\vec{q};z_1,z_2)\cong C_0(z_1)\delta(z_1-z_2)-\tfrac{1}{6}l^2(q^2-d^2/dz_1{}^2)\delta(z_1-z_2). \tag{21}$$

The first term $C_0(z)$ is related to the local compressibility of the fluid at density $n_0(z)$, or to the local Helmholtz free energy per particle, $a(n)$, at z,

$$kT(n^{-1}-C_0)=n^{-1}\partial p/\partial n=\partial^2 na(n)/\partial n^2. \tag{22}$$

The quantity l is a characteristic (Debye) length, of the order of the range of the direct correlation function. In this approximation, the density profile is determined by the differential equation

$$[\partial^2 n_0 a(n_0)/\partial n_0{}^2]\,dn_0/dz+\tfrac{1}{6}kTl^2 d^3n_0/dz^3=0. \tag{23}$$

One integration leads to an equation equivalent to the one used by Fisk and Widom,

$$\partial n_0 a(n_0)/\partial n_0+\tfrac{1}{6}kTl^2 d^2n_0/dz^2=\text{const.} \tag{24}$$

In the same approximation, $K_2(z_1,z_2)$ becomes $\tfrac{1}{6}l^2\delta(z_1-z_2)$, and the surface tension is given by

$$\alpha=\tfrac{1}{6}kTl^2\int dz\,[dn_0(z)/dz]^2. \tag{25}$$

This is equivalent to the formula used by Fisk and Widom in their theory of surface tension.

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[1] S. Fisk and B. Widom, J. Chem. Phys. 50, 3219 (1969).

[2] B. U. Felderhof, Physics (Long Is. City, N.Y.) 48, 541 (1970).

[3] F. P. Buff, R. A. Lovett, and F. H. Stillinger, Jr., Phys. Rev. Lett. 15, 621 (1965). See footnote 5 therein.

[4] It appears in an unpublished report of a talk given by J. Yvon at the International Union of Pure and Applied Physics Symposium on Thermodynamics, Brussels, 1948; we can find no reference to this in abstract journals or in the Science Citation Index. Also, it has been obtained independently (but not published) by F. P. Buff. (We are indebted to Professor Buff for calling attention to this prior work.)

[5] J. K. Percus, in *The Equilibrium Theory of Classical Fluids,* edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), pp. II-57 to II-61.

[6] This is the formula derived by Yvon. An apparently different expression has been given by F. P. Buff and R. A. Lovett, in *Simple Dense Fluids,* edited by H. L. Frisch and Z. W. Salsburg (Academic, New York, 1968). Professor Buff and Professor Lovett have both informed us that their formula can be transformed exactly into the one given in Eq. (20).

[7] J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 17, 338 (1949).

Early Departure from Free Acceleration and Turbulent Heating of Electrons in a Toroidal Experiment*

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Shortly after initiation of a high-voltage toroidal discharge in Ar, departure from free-electron acceleration is observed, together with electron heating such that the total energy input is accounted for. This early behavior is attributed to a high-frequency instability ($\omega_{pi}<\omega<\omega_{pe}$) due to interaction between relatively few trapped electrons and the streaming electrons.

In this paper we report an investigation of the early time behavior of a high-voltage, toroidal discharge. The transition from free-electron acceleration to acceleration at a reduced rate is observed, as well as the concurrent onset of turbulence and electron heating.

The experimental system has been described previously[1] in a report on the behavior of the dis-