Surface tension and energy of a classical liquid–vapour interface

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(Received 31 January 1977)

Rigorous general expressions for the surface tension \( \sigma \) and the surface energy per unit area \( \epsilon \) are derived in the form of three-fold integrals. In the approximation \( n(z_1) n(z_2) g(r_{12}, \bar{n}) \) we obtain the following results:

(i) Both \( \sigma \) and \( \epsilon \) are proportional to \((n_1 - n_v)^2\).
(ii) The expressions for \( \sigma \) and \( \epsilon \) are formally reduced to a single integral, with integrands determined in terms of the density profile \( n(z) \).
(iii) Explicit expressions are given for an exponential density variation.
(iv) In the limit of a density variation which is slow on the scale of the molecular diameter, we derive the general expressions \( \sigma = A(n_1 - n_v)^2/\lambda \), \( \epsilon = B(n_1 - n_v)^2/\lambda \) from the microscopic theory (\( \lambda \) is a measure of the surface thickness). The same forms for \( \sigma \) and \( \epsilon \) follow from (iii), with explicit expressions for \( A \) and \( B \). These forms for \( \sigma \) and \( \epsilon \) are shown to be very good approximations even well away from the critical point. It is argued that the critical power laws have the same range of validity.
(v) The critical exponents of \( A \) and \( B \) are determined, that for \( A \) agreeing with the result of Fisk and Widom. (vi) The surface thickness is determined for Ar, Kr and Xe near their triple points, using our theory for \( \epsilon \) and experimental data on the bulk energy of the liquids. The results are in excellent agreement with other estimates.

Similar results are obtained with the direct correlation function expression for the surface tension: the general expression is reduced to a three-fold integral, and results analogous to (i) through (iv) are obtained in the approximation \( c(r_1, r_2) = c(r_{12}, \bar{n}) \). The equivalence of the \( c(r_1, r_2) \) and \( g(r_1, r_2) \) formulations for \( \sigma \) is proved in the low density limit.

1. Summary of results

By using the thermodynamic definition \( \sigma = (\partial F/\partial A)_{V,T} \) of surface tension, and by extracting that part of the total energy which is proportional to the surface area, we obtain, for a liquid–vapour interface lying in the \( xy \) plane, and assuming the total potential energy has the form

\[
U(r_1, \ldots r_N) = \sum_{i<j} u(r_{ij}),
\]

\[
\sigma' = \frac{\pi}{2} \int_0^L \int_0^L \int_0^\infty \frac{dr}{|z_{1i}|} n_2(r, z_1, z_2) \frac{du}{dr} (r^2 - 3z_{1i}^2)
\]

and

\[
\epsilon' = \pi \int_0^L \int_0^L \int_0^\infty \frac{dr}{|z_{1i}|} n_2(r, z_1, z_2) ru(r).
\]

(The reason for the quotation marks is explained in the text.) In the approximation

\[
n_2(r, z_1, z_2) = n(z_1)n(z_2)g(r, \bar{n})
\]
we derive from (25) and (29) the expressions

\[ \sigma = \frac{\pi}{2} (n_1 - n_v)^2 \int_0^\infty dr \, g(r, \bar{n}) \frac{du}{dr} \left[ \frac{1}{4} r^4 + p_1(r) + p_2(r) \right] \]  

(50)

and

\[ \epsilon = \pi (n_1 - n_v)^2 \int_0^\infty dr \, g(r, \bar{n}) u(r) \left[ -\frac{1}{2} r^2 + q_1(r) + q_2(r) \right]. \]  

(69)

where the functions \( p_i \) and \( q_i \) are determined in terms of the density \( n(z) \). For an exponential density variation (characteristic length \( \lambda \)), these formulae give (with \( F = g(du/dr) \) and \( h = rgu \))

\[ \sigma = \frac{\pi}{2} (n_1 - n_v)^2 \int_0^\infty dr \, F(r) \left\{ \frac{1}{4} r^4 + \lambda^4 \left[ 18 - 2 \frac{r^2}{\lambda^2} - \exp (-r/\lambda) \left( 18 + 18 \frac{r}{\lambda} + 7 \frac{r^2}{\lambda^2} + \frac{r^3}{\lambda^3} \right) \right] \} \]  

(77)

and

\[ \epsilon = -\frac{\pi}{2} (n_1 - n_v)^2 \int_0^\infty dr \, h(r) \left\{ r^2 + \lambda^2 \left[ 4 - \exp (-r/\lambda) \left( 4 + \frac{r}{\lambda} \right) \right] \right\}. \]  

(78)

When \( \lambda \) is large these formulae simplify to

\[ \sigma = \frac{\pi}{30} (n_1 - n_v)^2 \frac{1}{\lambda} \int_0^\infty dr \, F(r) r^4, \]  

(80)

\[ \epsilon = -\frac{3\pi}{2} (n_1 - n_v)^2 \lambda \int_0^\infty dr \, h(r) r. \]  

(81)

A comparison of integrands shows that (80) and (81) are good approximations to (77) and (78) even when \( \lambda \) equals the core diameter. An alternative treatment for slowly varying density, based on a Taylor expansion of the density, gives

\[ \sigma = A(n_1 - n_v)^2 / \lambda \]  

(84)

and

\[ \epsilon = B(n_1 - n_v)^2 \lambda, \]  

(90)

where the coefficients \( A \) and \( B \) reduce to those of (80) and (81) for an exponential density variation.

In the limit \( \lambda \to 0 \) the expressions for \( \sigma \) and \( \epsilon \) are shown to be thermodynamically consistent (i.e. to satisfy \( \epsilon = \sigma - T(d\sigma/dT) \)) for a dilute gas–wall interface. The thermodynamic relation between \( \sigma \) and \( \epsilon \) leads to an equation for their critical exponents \( \mu \), \( \mu' \); namely

\[ \mu' = \mu - 1. \]  

(97)

This result is also derived by an extension of an argument due to Widom. The critical exponents \( \alpha' \), \( \beta' \), \( \nu \) and \( \gamma \) of \( A, B, \lambda^{-1} \) and \( \chi_T^{-1} \) are shown to satisfy

\[ \alpha' = \gamma - 2\nu \]  

(103)

\[ \beta' = \gamma - 1 \]  

(104)

The surface thickness (\( \simeq 2\lambda \)) of Ar, Kr and Xe is found from (81) and experimental data to be slightly larger than the molecular diameter near the triple point, in excellent agreement with the Egelstaff and Widom estimate.
Finally, similar results are obtained using the direct correlation function theory for the surface tension. The general expression corresponding to (25) is

\[
\sigma_c = \frac{\pi}{2} T \int_{-\infty}^{\infty} d z_1 \int_{-\infty}^{\infty} d z_2 \frac{d n(z_1)}{d z_1} \frac{d n(z_2)}{d z_2} \int_{|z_1|} d r r c(r, z_1, z_2) (r^2 - z_1 z_2^2). \tag{110}
\]

When the direct correlation function is approximated by \( c(r_1, n) \),

\[
\sigma_c = \frac{\pi}{2} T \int_{0}^{\infty} d r r c(r, n) \int_{-\infty}^{\infty} d z_1 \frac{d n(z_1)}{d z_1} \int_{z_1}^{z_1 + r} d z_2 \frac{d n(z_2)}{d z_2} (r^2 - z_1^2 z_2^2). \tag{113}
\]

For an exponential density variation,

\[
\sigma_c = \frac{\pi}{2} T (n_1 - n_v)^2 \int_{0}^{\infty} d r r c(r, n)
\times \left\{ r^2 - 4 \lambda^2 + \lambda^2 \exp \left( -r/\lambda \right) \left( 4 + 4 \frac{r^2}{\lambda^2} \right) \right\}, \tag{115}
\]

which becomes

\[
\sigma_c = \frac{\pi}{6} T (n_1 - n_v)^2 \int_{0}^{\infty} d r r^4 c(r, n) \tag{116}
\]

in the large \( \lambda \) limit. Corresponding to (84) we show that, for slowly varying density, \( \sigma_c = A_c (n_1 - n_v)^2 / \lambda \). The pair correlation and the direct correlation theories are proved to be equivalent to the lowest order in density, but the question of their equivalence in general is left open.

2. GENERAL EXPRESSIONS FOR SURFACE TENSION AND SURFACE ENERGY

Basically, there are two definitions of surface tension. One is the mechanical definition of \( \sigma \) as the stress transmitted across a strip of unit width normal to the interface, and the other is the thermodynamic definition as the isothermal change in the Helmholtz free energy during the formation (at constant volume) of a unit area of surface. The Kirkwood and Buff [1] general treatment used the mechanical definition, and their result was shown to be obtainable from the thermodynamic definition by Buff [2] and MacLellan [3]. These treatments arrive at a general expression for \( \sigma \) as a four-fold integral. We will give a simple derivation using the thermodynamic definition of \( \sigma \) and based on the deformation method of Harasima [4] and Toda [5]. This method is mathematically equivalent to that used by Buff and MacLellan, but is physically more transparent. We reduce the general expression for \( \sigma \) to a three-fold integral, and in addition obtain a general three-fold integral expression for the surface energy \( \epsilon \). (For some interesting alternative formulations of surface tension theory, see [6–8]).

From now on we consider a two-phase classical system of \( N \) atoms inside the box of figure 1. In the calculation of \( \sigma \) and \( \epsilon \) we assume that the only effect of gravity is to create a flat liquid–vapour interface. (Gravitational pressure gradients can be neglected experimentally for all temperatures such that \( |T_c - T| / T_c \) is greater than about \( 10^{-5} \); see Kadanoff et al. [9], p. 421.)

To change the area of the liquid–vapour interface without changing the total volume or the volume of either phase, we expand the box from \( L_1 \) to \( L_1 (1 + \xi) \) in...
the $x$-direction, and contract it from $L_3$ to $L_3(1 + \xi)^{-1}$ in the $z$-direction, leaving $L_3$ unchanged. The deformation is performed isothermally. The increase in the interface area is

$$\Delta A = L_1L_3(1 + \xi) - L_1L_2 = \xi L_1L_2.$$  \hfill (1)

From the thermodynamic definition of surface tension, $\sigma$ is contained within

$$\sigma = \lim_{\Delta A \to 0} \frac{\Delta F}{\Delta A},$$  \hfill (2)

where $\Delta F$ is the increase in the Helmholtz free energy. The reason for the inverted commas around $\sigma$ is that $\Delta F$ also contains terms due to the change in the liquid–wall and vapour–wall interfacial areas, and thus gives more than just the surface free energy of the liquid–vapour interface. We will continue to use this notation throughout the paper, finally doing away with the inverted commas when we have identified and discarded all the parts of $\Delta F$ which are not true interface terms. This procedure is required by the mathematical rigour which this subject demands (specifically by the need to keep the system under consideration finite so that interchange of order of integration can be done rigorously).

The free energy of the original system is given by ([10], Chap. 2, problem 33)

$$\exp \left( -\frac{F}{T} \right) = \frac{1}{N!} \left( \frac{mT}{2\pi\hbar^2} \right)^{3N/2} \int_0^{L_1} dx_1 \cdots \int_0^{L_2} dz_N \exp \left( -\frac{U(x_1 \cdots z_N)}{T} \right),$$  \hfill (3)

where $U$ is the total potential energy, and the temperature $T$ is given the dimension of energy. The free energy of the deformed system is given by

$$\exp \left( -\frac{F'}{T} \right) = \frac{1}{N!} \left( \frac{mT}{2\pi\hbar^2} \right)^{3N/2} \int_0^{L_1(1 + \xi)} dx_1 \cdots \int_0^{L_2(1 + \xi)^{-1}} dz_N \exp \left( -\frac{U(x_1 \cdots z_N)}{T} \right).$$  \hfill (4)

If we introduce the scaled coordinates

$$x' = \frac{x}{1 + \xi}, \quad y' = y, \quad z' = z(1 + \xi)$$  \hfill (5)
into (4), then integrations in the new coordinates have the same limits as in (3). The jacobian of this change of variables is unity, so

\[ \exp \left( -\frac{F'}{T} \right) = \frac{1}{N!} \left( \frac{mT}{2\pi\hbar^2} \right)^{3N/2} \int_0^{L_1} \ldots \int_0^{L_n} \int_0^{L_{N-1}} \int_0^{L_N} dx' \ldots dx_N \]

\[ \times \exp \left\{ -\frac{U(x_1'(1+\xi) \ldots x_N'(1+\xi)^{-1})}{T} \right\} \]

(6)

If we now set \( F' = F + \Delta F \) and

\[ U(x_1(1+\xi) \ldots x_N(1+\xi)^{-1}) = U(x_1 \ldots x_N) + \Delta U, \]

then to lowest order

\[ \Delta F = \frac{\int_0^{L_1} \ldots \int_0^{L_n} dx_1 \ldots dx_N \Delta U \exp \left( -\frac{U}{T} \right)}{\int_0^{L_1} \ldots \int_0^{L_n} dx_1 \ldots dx_N \exp \left( -\frac{U}{T} \right)} = \langle \Delta U \rangle. \]  

(8)

(The last equality defines expectation value brackets.) Note that the change in the free energy produced by this isothermal, constant volume deformation has the appearance of a change in the total energy of the system (the kinetic energy is isotropic in classical fluids, and is constant in isothermal deformations). This is deceptive, however: the total thermodynamic energy \( E \) is (for monatomic systems)

\[ E = \frac{3}{2} NT + \frac{1}{T} \int_0^{L_1} \ldots \int_0^{L_n} dx_1 \ldots dx_N \frac{U \exp \left( -\frac{U}{T} \right)}{\int_0^{L_1} \ldots \int_0^{L_n} dx_1 \ldots dx_N \exp \left( -\frac{U}{T} \right)} \]

\[ = \frac{3}{2} NT + \langle U \rangle. \]  

(9)

By the above arguments we find, for the same isothermal deformation,

\[ \Delta E = \langle \Delta U \rangle + \frac{1}{T} \{ \langle U \rangle \langle \Delta U \rangle - \langle U \Delta U \rangle \}, \]

so that

\[ \Delta E = \Delta \langle U \rangle \neq \langle \Delta U \rangle. \]

(10)

The second term in (10) gives the entropy change caused by the deformation, since

\[ E = F + TS, \Delta E = \Delta F + T \Delta S \] (isothermal change).

Returning to the expression (8) for \( \Delta F \), we see from (7) that

\[ \Delta U = \xi \sum_{j=1}^{N} \left( x_j \frac{\partial U}{\partial x_j} - z_j \frac{\partial U}{\partial z_j} \right) + O(\xi^2), \]

(13)

so that

\[ \langle \Delta U \rangle = N\xi \left( x_1 \frac{\partial U}{\partial x_1} - z_1 \frac{\partial U}{\partial z_1} \right) + O(\xi^2). \]

(14)
We now specialize to central pairwise forces, that is

\[ U = \sum_{i<j}^N u(r_{ij}), \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \]

Then

\[
\left\langle x_1 \frac{\partial U}{\partial x_1} \right\rangle = (N-1) \left\langle x_1 \frac{du(r_{12})}{dr_{12}} \right\rangle
\]

\[
= (N-1) \left( \frac{x_1 x_{12}}{r_{12}} \frac{du(r_{12})}{dr_{12}} \right)
\]

\[
= \frac{1}{3} (N-1) \left( \frac{x_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}} \right),
\]

where the last line follows from the equality of \( \left\langle x_1 \left( \frac{\partial U}{\partial x_1} \right) \right\rangle \) and \( \left\langle x_2 \left( \frac{\partial U}{\partial x_2} \right) \right\rangle \).

We thus have

\[
\left\langle \Delta U \right\rangle = \xi \frac{1}{2} N(N-1) \left( \frac{x_{12}^2 - z_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}} \right) + O(\xi^2),
\]

which we can write as

\[
\left\langle \Delta U \right\rangle = \xi \frac{1}{4} N(N-1) \left( \frac{r_{12}^2 - 3z_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}} \right) + O(\xi^2)
\]

because of the physical equivalence of the \( x \) and \( y \) directions. In terms of the pair density \( n_2 \) defined by

\[
n_2(r_{12}, z_1, z_2) = \frac{N(N-1)}{4L_1L_2} \int dr_1 \cdots \int dr_N \exp \left( -\frac{U}{T} \right)
\]

the surface tension becomes

\[
\sigma = \lim_{\xi \to 0} \frac{\left\langle \Delta U \right\rangle}{\xi L_1 L_2}
\]

\[
= \frac{1}{4L_1L_2} \int dr_1 \int dr_2 \ n_2(r_{12}, z_1, z_2) \frac{r_{12}^2 - 3z_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}}
\]

(This is easily transformed into the general expression of Kirkwood and Buff [1].) We can simplify this result by making use of the symmetry of the system, which implies that everywhere except near the walls of the box \( n_2 \) is function of only three variables \( r_{12}, z_1 \) and \( z_2 \):

\[
n_2(r_{12}, z_1, z_2) = n_2(r_{12}, z_1, z_2).
\]

Then making use of the identity [11]

\[
\int_0^L dx_1 \int_0^L dx_2 f(|x_{12}|) = 2L \int_0^L dx \left( 1 - \frac{x}{L} \right) f(x),
\]

we can perform two integrations immediately:

\[
\sigma = \int_0^{L_1} dx_1 \int_0^{L_2} dx_2 \int_0^{L_1} dx_1 \int_0^{L_2} dx_1 \left( 1 - \frac{x_{12}}{L_1} \right) \frac{r_{12}^2 - 3z_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}}
\]

\[
\times n_2(r_{12}, z_1, z_2) \frac{r_{12}^2 - 3z_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}}
\]
The terms \( x_{12}/L_1 \) and \( y_{12}/L_2 \) in the integrand can be identified as contributing only to the free energy of the liquid- and vapour-side wall interfaces. To see this, consider a fluid above its critical temperature: the pair density becomes \( n_x=n^2g(r) \), where \( n \) is the density of the single phase filling the box. The change in free energy caused by the deformation of this single-phase system is (cf. (22))

\[
\Delta F = 2n^2\xi L_1 L_2 L_3 \int_0^L dx_{12} \left( 1 - \frac{x_{12}}{L_1} \right) \int_0^L dy_{12} \left( 1 - \frac{y_{12}}{L_2} \right) \int_0^L dz_{12} \times \left( 1 - \frac{z_{12}}{L_3} \right) g(r) \frac{r^2-3z_{12}^2}{r} \frac{du}{dr},
\]

where we have dropped the suffix 12 on \( r \). The term in \( x_{12}/L_1 \) is thus proportional to \( \xi L_2 L_3 \) (there are also \( \xi L_2 \), \( \xi L_3 \) and \( \xi \) terms which we can neglect) and therefore corresponds to a change in the \( yz \)-wall area. Thus we can discard the \( x_{12}/L_1 \) and \( y_{12}/L_2 \) terms, and (22) reduces to

\[
\sigma' = \int_0^L dx_1 \int_0^L dz_2 \int_0^\infty dx_{12} \int_0^\infty dy_{12} n_2(r, z_1, z_2) \frac{r^2-3z_{12}^2}{r} \frac{du}{dr},
\]

where we have dropped the suffix 3 on \( L_3 \), and extended the range of the \( x_{12} \) and \( y_{12} \) integrations to infinity. The latter is valid on the assumption that the force factor \( du/dr \) limits contributions to the integral to microscopic values of \( r \) (and therefore of \( x_{12} \) and \( y_{12} \)).

We can now perform one more integration by changing from \( x_{12} \), \( y_{12} \) to the cylindrical coordinates \( \rho \) and \( \phi \):

\[ x_{12} = \rho \cos \phi, \quad y_{12} = \rho \sin \phi, \quad dx_{12} dy_{12} = \rho \, d\rho \, d\phi. \]

Then (24) becomes

\[
\sigma' = \frac{\pi}{2} \int_0^L dx_1 \int_0^L dz_2 \int_0^\infty d\rho \, n_2(r, z_1, z_2) (r^2-3z_{12}^2) \frac{du}{dr},
\]

and we have the surface tension reduced to a three-fold integral. The reason for keeping the quotation marks around \( \sigma \) is that (25) still contains 'floor' and 'ceiling' terms. These will be identified and discarded in §3.

We now consider the surface energy, i.e. the surface part of the total thermodynamic energy \( E \) defined in equation (9). For pairwise central interactions, (9) reduces to the well-known expression

\[
E = \frac{3}{2} NT + \frac{1}{2} \int dr_1 \int dr_2 n_2(r_1, r_2) u(r_{12}).
\]

For a classical system, the kinetic energy density is constant, i.e. there is no kinetic contribution to the surface energy (this is not so for a quantum system). Thus the surface energy per unit area \( \epsilon \) is \( (L_1 L_2)^{-1} \) times the surface part of the potential energy

\[
\langle U \rangle = \frac{1}{2} \int dr_1 \int dr_2 n_2(r_1, r_2) u(r_{12}).
\]

Instead of deforming the box to extract the surface part (i.e. evaluating (10) explicitly), we prefer instead to extract the term proportional to \( L_1 L_2 \) directly
from (27). When the liquid–vapour interface lies in the \( x'y' \) plane \( n_2=n_2(z_{12}, z_1, z_2) \) and

\[
\langle U \rangle = 2L_1L_2 \int_0^{L_1} dx_{12} \left( 1 - \frac{x_{12}}{L_1} \right) \int_0^{L_2} dy_{12} \left( 1 - \frac{y_{12}}{L_2} \right) \times \int_0^{L_1} dz_1 \int_0^{L_2} dz_2 n_2(r, z_1, z_2)u(r). \tag{28}
\]

As noted for the free energy, the \( x_{12}/L_1 \) and \( y_{12}/L_2 \) terms do not lead to liquid–vapour interface energies, so

\[
\pi = \int_0^{L_1} dz_1 \int_0^{L_2} dz_2 \int_0^{\infty} dy_{12} n_2(r, z_1, z_2)u(r)
\]

\[
= \pi \int_0^{L_1} dz_1 \int_0^{L_2} dz_2 \int_{|z|}^{\infty} dr n_2(r, z_1, z_2)u(r). \tag{29}
\]

The quotation marks are again necessary because (29) includes floor and ceiling surface terms (as for ' \( \sigma \)') and also, unlike the expression for ' \( \sigma \)', volume terms for the two phases.

3. RESULTS BASED ON THE APPROXIMATION \( n_2 = n(z_1)n(z_2)g(r_{12}, \bar{n}) \)

The probability of simultaneously finding a particle centred in volume element \( dr_1 \) about \( r_1 \) and another centred in \( dr_2 \) about \( r_2 \) is \( n_2(r_1, r_2) dr_1 dr_2 \), as can be seen directly from the definition of \( n_2 \), equation (18). The probability of finding a particle centred in \( dr_1 \) about \( r_1 \) is \( n(r_1) dr_1 \), where \( n(r_1) \) is the single density. Thus the joint probability \( n_2(r_1, r_2) dr_1 dr_2 \) must be proportional to the product of \( n(r_1) dr_1 \) and \( n(r_2) dr_2 \) and a generalized pair-correlation function \( g(r_1, r_2) \):

\[
n_2(r_1, r_2) = n(r_1)n(r_2)g(r_1, r_2). \tag{30}
\]

However, \( g(r_1, r_2) \) is not known for a system with density gradients. Some writers [8, 12] make the approximation

\[
g(r_1, r_2) \approx g_1(r_{12}), \tag{31}
\]

where \( g_1 \) is the pair-correlation function deep inside the liquid phase. We will make the slightly less restrictive approximation

\[
g(r_1, r_2) \approx g(r_{12}, \bar{n}), \tag{32}
\]

where \( \bar{n} \) is some average density to be chosen on physical grounds. For example, near the critical point an obvious choice is \( \bar{n} = \frac{1}{2}(n_1 + n_v) \), while near the triple point \( \bar{n} \) tends to \( n_1 \), since correlations in the very dilute gas phase are then unimportant. Some justification for this type of approximation has been given by means of functional differentiation [13], and it is also clear that (32) is correct to the lowest order in density, since (cf. Kubo [10], Chap. 5, problem 22)

\[
g(r_1, r_2) = \exp \left( -\frac{u(r_{12})}{T} \right) \cdot \{1 + \text{terms of higher order in density}\}, \tag{33}
\]

irrespective of inhomogeneities in the system. The choice of \( \bar{n} \) can be avoided in numerical work such as the Monte Carlo approach of Freeman and McDonald.
[14], who use expressions derived on the assumption \( g(r_1, r_2) = g(r_{12}) \), but do not deal with \( g(r) \) directly. Rather, they generate configurations (with probability \( \exp(-U/T) \)) consistent with a given density profile. Of course, approximations like (32) can be avoided altogether if the numerical work is based on the exact expressions (25) and (29).

We now proceed to evaluate \( \sigma \) and \( \epsilon \) using

\[
n_d(r_{12}, z_1, z_2) = n(z_1)n(z_2)g(r_{12}, \bar{n}).
\]

From (25) and (34) we have

\[
\sigma = \frac{\pi}{2} n_v^2 \int_0^L dz_1 n(z_1) \int_0^L dz_2 n(z_2) \int_{|z_1|}^{\infty} dr F(r)(r^2 - 3z_{12}^2),
\]

where

\[
F(r) = g(r, \bar{n}) \frac{du}{dr}
\]

is (apart from the sign) the average force between two particles in the fluid separated by distance \( r \). We now write

\[
n(z) = n_v + (n_1 - n_v)f(z),
\]

where \( f(z) \) tends to unity deep in the liquid and to zero far in the gas.

Then

\[
\sigma = \frac{\pi}{2} n_v^2 \int_0^L dz_1 n(z_1) \int_0^L dz_2 n(z_2) \int_{|z_1|}^{\infty} dr F(r)(r^2 - 3z_{12}^2)
+ \frac{\pi}{2} n_v(n_1 - n_v) \int_0^L dz_1 \int_0^L dz_2 [f(z_1) + f(z_2)] \int_{|z_1|}^{\infty} dr F(r)(r^2 - 3z_{12}^2)
+ \frac{\pi}{2} (n_1 - n_v)^2 \int_0^L dz_1 f(z_1) \int_0^L dz_2 f(z_2) \int_{|z_1|}^{\infty} dr F(r)(r^2 - 3z_{12}^2).
\]

Using (21) we see that the first term equals

\[
\pi n_v^2 L \int_0^\infty dz \left( 1 - \frac{z}{L} \right) \int_{|z|}^{\infty} dr F(r)(r^2 - z^2) = \frac{\pi}{4} n_v^2 \int_0^\infty dr r^4 F(r).
\]

We note for comparison the Fowler formula [15] which was derived using the approximations \( n_v = 0 \), \( g(r_1, r_2) = g_1(r) \), namely

\[
\sigma_v = \frac{\pi}{8} n_v^2 \int_0^\infty dr F_1(r)r^4.
\]

Thus (39) represents the surface free energy of the interfaces between a vapour phase and the top and bottom of the box. We therefore discard the first term in (38), since it does not arise from the presence of a liquid–vapour interface.

Turning to the second term in (38), we note that it is proportional to

\[
\int_0^L dz_1 f(z_1) \int_0^L dz_2 \int_{|z_1|}^{\infty} dr F(r)(r^2 - 3z_{12}^2)
= \int_0^L dz_1 f(z_1) \int_{z_1}^{\infty} dr F(r)z_1(r^2 - z_1^2).
\]
(We have used the fact that \( F(r) \) goes to zero in a microscopic distance, plus the presence of \( f(z_1) \), to extend the range of \( z_2 \) to infinity in carrying out the integration.) Because of \( F \), the contributions to (41) come only from small \( z_1 \), i.e. from near the bottom of the tank. Thus we discard the second term in (38), and are left with
\[
\sigma' = \frac{\pi}{2} (n_1 - n_v)^2 \int_0^L dz_1 f(z_1) \int_0^L dz_2 f(z_2) \int_{|z_{1s}|}^{\infty} dr F(r) (r^2 - 3z_{1s}^2). \tag{42}
\]
We have kept the quotation marks around \( \sigma' \) because there is still one spurious term to be discarded. This can be seen as follows: we write
\[
f(z) = f_D(z) + \delta f(z), \tag{43}
\]
where \( f_D(z) \) is a step function,
\[
f_D(z) = \begin{cases} 1 & z \leq D \\ 0 & z > D \end{cases} \tag{44}
\]
and the range of \( \delta f(z) \) is the surface thickness. The contribution to (42) from the term \( f_D(z_1)f_D(z_2) \) is of the same form as the first term in (38), with \( L \) replaced by \( D \), and thus equals
\[
\frac{\pi}{4} (n_1 - n_v)^2 \int_0^\infty dr F(r)r^4.
\]
As with (39) this has combined two equal terms, one from the liquid–vapour interface \( (z_1 \approx D \approx z_2) \) and the other from the bottom of the tank \( (z_1 \text{ and } z_2 \text{ both near zero}) \). All other contributions to (42) are true interface terms since they involve \( \delta f \)'s. Thus we have, finally without quotation marks
\[
\sigma = \frac{\pi}{8} (n_1 - n_v)^2 \int_0^\infty dr F(r)r^4
\]
\[+ \frac{\pi}{2} (n_1 - n_v)^2 \int_0^L dz_1 \delta f(z_1) \int_{|z_{1s}|}^{D} dz_2 \int_{|z_{1s}|}^{\infty} dr F(r) (r^2 - 3z_{1s}^2) \]
\[+ \frac{\pi}{2} (n_1 - n_v)^2 \int_0^L dz_1 \delta f(z_1) \int_{|z_{1s}|}^{L} dz_2 \delta f(z_2) \int_{|z_{1s}|}^{\infty} dr F(r) (r^2 - 3z_{1s}^2) \tag{45}
\]
When \( n_v \) is negligible the first term reduces to the Fowler expression (40). For the second term we find
\[
\int_{|z_{1s}|}^{D} dz_2 \int_{|z_{1s}|}^{\infty} dr F(r) (r^2 - 3z_{1s}^2) = - \int_{|z_{1s}|}^{-|z_{1s} - D|} dr F(r)(z_1 - D)^2. \tag{46}
\]
It is now convenient to change to a height coordinate which has the surface at the origin: we put
\[ \zeta = z - D \text{ and } \delta f(z) = \delta f(\zeta). \] (47)

Using (46), (47) and the fact that \( D \) and \( L - D \) are macroscopic lengths, we obtain for the second term in (45)
\[ -\pi(n_1 - n_v)^2 \int_{-\infty}^{\infty} d\zeta \delta f(\zeta) \zeta \int_{|\zeta|}^{\infty} dr F(r)(r^2 - \zeta^2) \]
\[ = -\pi(n_1 - n_v)^2 \int_{0}^{\infty} dr F(r) \int_{-r}^{r} d\zeta \delta f(\zeta)(r^2 - \zeta^2). \] (48)

In the last term of (45) we have
\[ \int_{-\infty}^{\infty} d\zeta_1 \delta f(\zeta_1) \int_{-\infty}^{\infty} d\zeta_2 \delta f(\zeta_2) \int_{|\zeta_1|}^{\infty} dr F(r)(r^2 - 3\zeta_{12}^2) \]
\[ = \int_{-\infty}^{\infty} d\zeta_1 \delta f(\zeta_1) \int_{0}^{\infty} dr F(r) \int_{-r}^{r} d\zeta_2 \delta f(\zeta_2)(r^2 - 3\zeta_{12}^2) \]
\[ = \int_{0}^{\infty} dr F(r) \int_{-r}^{r} d\zeta_1 \delta f(\zeta_1) \int_{-r}^{r} d\zeta_2 \delta f(\zeta_2)(r^2 - 3\zeta_{12}^2). \] (49)

Combining these results gives
\[ \sigma = \frac{\pi}{2} (n_1 - n_v)^2 \int_{0}^{\infty} dr F(r) \left[ \frac{1}{4} r^4 + p_1(r) + p_2(r) \right], \] (50)
where
\[ p_1(r) = -2 \int_{-r}^{r} d\zeta \delta f(\zeta)(r^2 - \zeta^2), \]
\[ p_2(r) = \int_{-\infty}^{\infty} d\zeta_1 \delta f(\zeta_1) \int_{-r}^{r} d\zeta_2 \delta f(\zeta_2)(r^2 - 3\zeta_{12}^2). \] (51)

Note that we have proved, in the approximation \( n_\alpha(r, z_1, z_2) = n(z_1)n(z_2)g(r_{12}, \bar{n}) \), that the surface tension is proportional to \((n_1 - n_v)^2\). This result shows a desired symmetry between the liquid and vapour phases. MacLellan [3] has previously suggested a similar extension to the Fowler formula, namely
\[ \sigma = \frac{\pi}{8} \int_{0}^{\infty} dr \frac{du}{dr} r^4 \left[ n_1 g(r)^{1/2} - n_v g(r)^{1/2} \right]^2, \]
which gives the first term of (50) on the assumption that
\[ g(r, n_1) = g(r, n_v) = g(r, \bar{n}). \]

We now turn to the energy per unit area of the interface, or briefly, the surface energy. From the general expression for \( \epsilon' \), equation (29), and using the approximation
\[ n_2 = n(z_1)n(z_2)g(r_{12}, \bar{n}), \]
we have
\[ \epsilon' = \pi \int_{0}^{L} d\bar{z}_1 n(z_1) \int_{0}^{L} d\bar{z}_2 n(z_2) \int_{|\bar{z}_{12}|}^{\infty} dr h(r). \] (52)
where
\[ h(r) = g(r, \tilde{n})ru(r). \] (53)

Like \( F(r) \), \( h(r) \) goes to zero rapidly over a microscopic range. We write, as before
\[ n(z) = n_v + (n_1 - n_v)\left[ f_D(z_1) + \delta f(z_2) \right]. \]

Then
\[ \epsilon' = \epsilon_0 + \epsilon_1 + \epsilon_2, \] (54)

where \( \epsilon_0, \epsilon_1, \) and \( \epsilon_2 \) come respectively from the \( n(z_1)n(z_2) \) terms
\[ (n_v + (n_1 - n_v)f_D(z_1))[n_v + (n_1 - n_v)f_D(z_2)], \]
\[ (n_1 - n_v)[n_v + (n_1 - n_v)f_D(z_1)] \delta f(z_2) + \delta f(z_2)[n_v + (n_1 - n_v)f_D(z_2)], \] (55)

and
\[ (n_1 - n_v)^2 \delta f(z_1) \delta f(z_2). \]

Thus
\[ \epsilon_0 = \pi \left\{ n_1^2 \int_0^D \int_0^D dz_1 \int_0^D dz_2 + 2n_1n_v \int_0^L \int_0^L dz_1 \int_0^L dz_2 \right. \]
\[ + n_v^2 \int_0^L \int_0^L dz_1 \int_0^L dz_2 \left\} \int_{z_1}^\infty dr h(r). \] (56)

Consider the first term of \( \epsilon_0 \). It is equal to (using (21) again)
\[ \pi n_1^2 2D \int_0^D dz \left( 1 - \frac{z}{D} \right) \int_{z_1}^\infty dr h(r) \]
\[ = D2n_1^2 \int_0^\infty dr h(r)r - \pi n_1^2 \int_0^\infty dr h(r)r^2. \] (57)

The first part of (57) is not a surface energy of any kind, but rather the bulk energy of the liquid phase divided by \( L_1L_2 \). The second part is twice the amount obtained in Fowler's approximation (Kirkwood and Buff [1], equation (31))
\[ \epsilon_F = -\frac{\pi}{2} n_1^2 \int_0^\infty dr h(r)r^2 \]
because it contains two contributions—one from the change in density at the bottom of the box, and an equal contribution coming from the liquid–vapour interface. (This is in exact correspondence to the discussion of the similar surface tension contributions.) Thus the first and last terms of (56) give a contribution to \( \epsilon_0 \) adding to
\[ -\frac{\pi}{2} (n_1^2 + n_v^2) \int_0^\infty dr h(r)r^2. \] (58)

The middle term of (56) is entirely a true liquid–vapour interface term, and equals
\[ \pi n_1 n_v \int_0^\infty dr h(r)r^2. \] (59)

Thus the liquid–vapour interface part of \( \epsilon_0 \) is
\[ \epsilon_0 = -\frac{\pi}{2} (n_1 - n_v)^2 \int_0^\infty dr h(r)r^2. \] (60)
Turning to $\epsilon_1$ and $\epsilon_2$, we note that the presence of the $\delta f$'s in the second and third part of (55) guarantees that only liquid–vapour interface terms are present. We have

$$
\epsilon_1 = 2\pi (n_1 - n_\nu) \left\{ n_1 \int_0^D dz_1 + n_\nu \int_D^L dz_1 \right\} \int_0^L dz_2 \delta f(z_2) \int_{|z_1|}^{\infty} dr h(r) \\
= 2\pi (n_1 - n_\nu) \left\{ n_1 J_1 + n_\nu J_\nu \right\}.
$$

(61)

The integrals $J_1$ and $J_\nu$ can be reduced as follows. We first change the order of the $z_1$ and $z_2$ integrations, then introduce the $\zeta$-coordinates defined in (47), then interchange the order of the $\zeta_1$ and $r$ integrations, carry out the $\zeta_1$ integration, and finally interchange the order of the $r$ and $\zeta_2$ integrations. We find

$$
J_1 = \int_0^\infty dr h(r) \left\{ - \int_{-r}^r d\zeta \tilde{\delta f}(\zeta) \zeta + r \left[ \int_{-r}^r d\zeta \tilde{\delta f}(\zeta) + 2 \int_{-\infty}^r d\zeta \tilde{\delta f}(\zeta) \right] \right\}
$$

(62)

and

$$
J_\nu = \int_0^\infty dr h(r) \left\{ + \int_{-r}^r d\zeta \tilde{\delta f}(\zeta) \zeta + r \left[ \int_{-r}^r d\zeta \tilde{\delta f}(\zeta) + 2 \int_{-\infty}^r d\zeta \tilde{\delta f}(\zeta) \right] \right\}.
$$

(63)

So far we have not specified the location of the surface. Ono and Kondo [16], pp. 139–142 (see also the discussion following equation (1) in Fisk and Widom [17]) point out that when the surface $(x=D)$ is chosen to be the Gibbs' dividing surface of vanishing superficial density (sometimes called the equimolecular dividing surface), then the surface tension becomes the superficial density of the Helmholtz free energy and there is a thermodynamic relation between $\sigma$ and $\epsilon$ analogous to that between $F$ and $E$. The location of the equimolecular dividing surface is determined by

$$
\int_0^D dz [n(z) - n_1] + \int_D^L dz [n(z) - n_\nu] = 0
$$

(64 a)

or equivalently

$$
\int_{-\infty}^{\infty} d\zeta \tilde{\delta f}(\zeta) = 0.
$$

(64 b)

This choice for $D$ leads to considerable simplification in $\epsilon$. For, using (64 b), we find

$$
J_1 + J_\nu = 0
$$

(65)

and $\epsilon_1$ simplifies to

$$
\epsilon_1 = 2\pi (n_1 - n_\nu)^2 \int_0^\infty dr h(r) \left\{ - \int_{-r}^r d\zeta \tilde{\delta f}(\zeta) \zeta + r \left[ \int_{-r}^r d\zeta \tilde{\delta f}(\zeta) + \int_{-\infty}^r d\zeta \tilde{\delta f}(\zeta) \right] \right\}
$$

(66)

We come finally to $\epsilon_2$, given by

$$
\epsilon_2 = \pi (n_1 - n_\nu)^2 \int_{-\infty}^\infty d\zeta_1 \tilde{\delta f}(\zeta_1) \int_{-\infty}^\infty d\zeta_2 \tilde{\delta f}(\zeta_2) \int_{|\zeta_1|}^{\infty} dr h(r).
$$

(67)

By the same steps as used in the reduction of the last term of (45), this can be written as

$$
\epsilon_2 = \pi (n_1 - n_\nu)^2 \int_0^\infty dr h(r) \int_{-\infty}^{\zeta_1+r} d\zeta_1 \tilde{\delta f}(\zeta_1) \int_{\zeta_1-r}^{\zeta_1+r} d\zeta_2 \tilde{\delta f}(\zeta_2).
$$

(68)
Thus, provided (64) holds,
\[ \epsilon = \pi (n_1 - n_\nu)^2 \int_0^\infty dr h(r) \left[ -\frac{1}{2} r^2 + q_1(r) + q_2(r) \right], \] (69)
where
\[ q_1(r) = -2 \int_r^\infty d\zeta \tilde{\delta f}(\zeta) \zeta - 2r \left[ \int_r^\infty d\zeta \tilde{\delta f}(\zeta) - \int_\infty^r d\zeta \tilde{\delta f}(\zeta) \right], \] (70)
\[ q_2(r) = \int_\infty^{-r} d\zeta_1 \tilde{\delta f}(\zeta_1) \int_{\zeta_1}^{\zeta_1+r} d\zeta_2 \tilde{\delta f}(\zeta_2). \]
We note that the choice (64) for the dividing surface has made \( \epsilon \) proportional to \( (n_1 - n_\nu)^2 \), in parallel to the dependence of \( \sigma \). This will prove to be important in the discussion of critical exponents in \( \S \ 7 \).

4. EXPONENTIAL DENSITY VARIATION

In the previous section we derived, in the approximation \( n = n(z_1)n(z_2)g(r, \vec{n}) \), expressions for \( \sigma \) and \( \epsilon \) that are valid for any variation of the density. We now give analytic results for the surface tension and the surface energy for a simple exponential variation of the density, namely
\[ n(\zeta) = \begin{cases} n_1 - \frac{1}{2}(n_1 - n_\nu) \exp(\zeta/\lambda), & \zeta < 0, \\ n_\nu + \frac{1}{2}(n_1 - n_\nu) \exp(-\zeta/\lambda), & \zeta > 0, \end{cases} \] (71)
where \( \lambda \) is a measure of the surface width. The density and its derivative are continuous at \( \zeta = 0 \), where
\[ n(0) = \frac{1}{2}(n_1 + n_\nu), \quad n'(0) = -\frac{1}{2}(n_1 - n_\nu)/\lambda. \] (72)
The function \( \tilde{\delta f} \) corresponding to this choice of density is
\[ \tilde{\delta f}(\zeta) = \frac{1}{2} \text{sgn} \ z \exp(-|\zeta|/\lambda), \] (73)
and, being odd, satisfies (64) automatically.

That this choice is correct at large \( |\zeta| \) (at least near the critical point) has been shown by Fisk and Widom [17] from a generalized van der Waals theory. The exponential density variation has also been used by Berry et al. [12], and Freeman and McDonald [14].

The evaluation of \( p_1 \) and \( q_1 \) from (51) and (70) is straightforward. We find
\[ p_1(r) = \lambda^4 \left[ 12 - 2 \left( \frac{r}{\lambda} \right)^2 \exp(-r/\lambda) \left( 12 + 12 \frac{r}{\lambda} + 4 \frac{r^2}{\lambda^2} \right) \right], \] (74)
\[ q_1(r) = -2\lambda^4 \left[ 1 - \exp(-r/\lambda) \right]. \]
Both \( p_1 \) and \( q_1 \) are zero at \( r = 0 \), and are otherwise negative and monotonically decreasing. The evaluation of \( p_2 \) and \( q_2 \) is made easier by noting that
\[ \frac{dq_2}{dr} = \int_{-\infty}^{\infty} d\zeta \tilde{\delta f}(\zeta) \left[ \tilde{\delta f}(\zeta + r) + \tilde{\delta f}(\zeta - r) \right] \]
\[ = 2 \int_{-\infty}^{\infty} d\zeta \tilde{\delta f}(\zeta) \tilde{\delta f}(\zeta + r) \quad \text{(for \( \tilde{\delta f} \) odd)} \]
\[ = \frac{1}{2} \lambda \exp(-r/\lambda)(1 - r/\lambda). \]
Thus

\[ q_2(r) = \frac{1}{2} \lambda r \exp \left( -r/\lambda \right). \]  

(75)

Similarly

\[ p_2(r) = r^2 q_2(r) - 3 I(r), \]

where

\[ I(r) = \int_{-\infty}^{\infty} d\zeta \delta f(\zeta) \int_{-r}^{r} dz \zeta^2 \delta f(\zeta + z), \]

so that

\[ \frac{dI}{dr} = r^2 \frac{dq_2}{dr}, \]

thus

\[ p_2(r) = \lambda^2 \left[ 6 - \exp \left( -r/\lambda \right) \left( 6 + 6 \frac{r}{\lambda^2} + \frac{r^2}{\lambda^4} \right) \right]. \]  

(76)

Both \( p_2 \) and \( q_2 \) are zero at \( r = 0 \) and are otherwise positive. While \( p_2 \) is monotonically increasing, \( q_2 \) has a maximum at \( r = \lambda \). The sums \( p_1 + p_2 \) and \( q_1 + q_2 \) are both monotonically decreasing.

Using these results we find, for this one-parameter density,

\[ \sigma = \pi \left( n_1 - n_\nu \right)^2 \int_0^\infty dr F(r) \left\{ \frac{1}{2} r^4 + \lambda^4 \left[ 18 - 2 \frac{r^2}{\lambda^2} - \exp \left( -r/\lambda \right) \right. \right. \]

\[ \times \left. \left. \left( 18 + 18 \frac{r}{\lambda} + 7 \frac{r^2}{\lambda^2} + 3 \frac{r^3}{\lambda^3} \right) \right] \right\} \]  

(77)

and

\[ \epsilon = -\frac{\pi}{2} \left( n_1 - n_\nu \right)^2 \int_0^\infty dr h(r) \left\{ \frac{1}{2} r^2 + \frac{4}{\lambda} \left[ 4 - \exp \left( -r/\lambda \right) \left( 4 + \frac{r}{\lambda} \right) \right] \right\}. \]  

(78)

The result for \( \epsilon \) is new; the expression for \( \sigma \) differs from that obtained by Berry et al. [12] only in the replacement of \( n_1^2 \) by \( (n_1 - n_\nu)^2 \). (This difference, of course, proves to be very important near the critical point.)

We consider the two limiting forms of \( \sigma \) and \( \epsilon \). The limit \( \lambda \to 0 \) (step function density) has \( \delta f \equiv 0 \), so from either (50) and (69) or from (77) and (78) we have

\[ \sigma_0 = \frac{\pi}{2} \left( n_1 - n_\nu \right)^2 \int_0^\infty dr F(r)r^4, \quad \epsilon_0 = -\frac{\pi}{2} \left( n_1 - n_\nu \right)^2 \int_0^\infty dr h(r)r^2. \]  

(79)

Neither of these expressions could be expected to be accurate, even near the triple point, since the thickness of the interface (approximately given by \( |\Delta n'| = 2\lambda \)) is unlikely to be much smaller than molecular size. Surprisingly, Freeman and McDonald [14] found numerical values of \( \sigma_0 \) quite close to the triple point experimental values for argon and neon (see also Berry et al. [12]). The reason for this is accidental, as can be seen from figure 3. There we have plotted as the full and dotted lines the integrand of the expression (77) for \( \sigma \), taking

\[ u(r) = 4u \left[ \left( \frac{d}{r} \right)^{12} - \left( \frac{d}{r} \right)^6 \right] \]

and \( g = \exp \left( -u/T \right) \).

The curves are for \( \lambda = d \) (\( d \) is the core diameter, which is plausibly about half the interface thickness \( 2\lambda \) near the triple point), and for \( \lambda = 0 \). We see that there is
a large degree of cancellation between positive and negative parts of the integrand in both cases, and that (for a more accurate \( g \)) \( \sigma_0 \) happens to give a good value only because of this cancellation, since the integrand is quite different numerically from that with \( \lambda = d \).

**Figure 3.** Integrands of the exponential density expressions for \( \sigma \) when \( \lambda = d \) with \( u(r) = 4v[(d/r)^{12}-(d/r)^6] \), \( g = \exp(-u/T) \). The value of \( 4v/T \) was taken to be 5.69, which is the average of the rare-gas triple-point values [28]. Full curve: general expression (77). Dashed curve: large \( \lambda \) expression (80). Dotted curve: \( \lambda = 0 \) limit (79). The area under a curve times \( (\pi/2)(n_1-n_v)^2d^2v \) gives the surface tension.

On the other hand, \( \epsilon_0 \) gives poor values for the surface energy [14]. The reason for this can be seen in figure 4, where we have plotted the integrand of the expression (78) for \( \epsilon \) for \( \lambda = d \) and \( \lambda = 0 \). In this case there is almost no cancellation between the positive and negative parts of the integrand, so that \( \epsilon_0 \) is far
from the experimental value, even at the triple point. We can further see from figures 3 and 4 that $\sigma_0 > \sigma$ and $\epsilon_0 < \epsilon$, as found by Freeman and McDonald [14].

![Figure 4](image)

**Figure 4. Integrands of the exponential density expressions for $\epsilon$, when $\lambda = d$ with $u, g$ and $v/T$ as in figure 3. Full curve: general expression (78). Dashed curve: large $\lambda$ expression (81). Dotted curve: $\lambda = 0$ limit (79). The area under a curve times $(\pi/2)(n_1 - n_\nu)^2 d^4 v$ gives the surface energy.**

We now look at the limit where $\lambda$ is large compared to the molecular size. This limit is of course attained as the critical point is approached, but expressions for large $\lambda$ prove to be surprisingly useful, even well away from the critical point. Since $F$ and $h$ rapidly become negligible as $r/d$ becomes large, the values of $r$ of importance in the integrand are then small compared with $\lambda$. Thus we can expand the integrands in $\sigma$ and $\epsilon$ as a series in $r/\lambda$. The leading terms for large $\lambda$ are

$$
\sigma = \frac{\pi}{30} (n_1 - n_\nu)^2 \frac{1}{\lambda} \int_0^\infty dr \ F(r)r^2
$$

and

$$
\epsilon = -\frac{3\pi}{2} (n_1 - n_\nu)^2 \lambda \int_0^\infty dr \ h(r)r.
$$

Thus the surface tension and surface energy are proportional to $\lambda^{-1}$ and $\lambda$ for large $\lambda$. We will obtain these results in another way in the next section.
It is interesting to compare the integrands of the expressions for $\sigma$ and $\epsilon$ in the large $A$ limit with those for $A \to 0$ and the full expressions given by (77) and (78). The large $A$ limit, evaluated at $A = d$, is shown as the dashed curve in figures 3 and 4. The agreement between the large $A$ limits and the full expressions is surprisingly good. In § 8 we will use this to extract the surface thickness from experimental data near the triple point.

5. SLOWLY VARYING DENSITY

It is possible to obtain general expressions for $\sigma$ and $\epsilon$ when the density variation is slow on the scale of the molecular diameter. The results given below are generalizations of the large $A$ limit of the exponential density variation. Consider the surface tension first, starting from (35):

$$\sigma = \frac{\pi}{2} \int_0^L dz_1 n(z_1) \int_0^L dz_2 n(z_2) \int_{|z_1|}^\infty dr F(r)(r^2 - 3z_1^2)$$

$$= \frac{\pi}{2} \int_0^L dz_1 n(z_1) \int_{-z_1}^{L-z_1} dz n(z_1 + z) \int_{|z|}^\infty dr F(r)(r^2 - 3z^2)$$

$$= \frac{\pi}{2} \int_0^L dz_1 n(z_1) \int_{-z_1}^{L-z_1} dz \left[n(z_1) + zn'(z_1) + \frac{1}{2}z^2 n''(z_1) + \ldots\right] \int_{|z|}^\infty dr F(r)$$

$$\times (r^2 - 3z^2).$$  (82)

Taking the $z$ integrals in turn, we see that because

$$\int_{-\infty}^{\infty} dz \int_{|z|}^\infty dr F(r)(r^2 - 3z^2) = \int_0^\infty dr F(r) \int_{-r}^r dz (r^2 - 3z^2) = 0,$$

the zeroth term in the Taylor expansion contributes only if $z_1$ is near 0 or $L$, and thus is not a liquid–vapour interface term. The second term similarly contains no interface contribution, since

$$\int_{-\infty}^{\infty} dz \int_{|z|}^\infty dr F(r)(r^2 - 3z^2) = 0.$$

Thus we are left with

$$\sigma = \frac{\pi}{4} \int_0^L dz_1 n(z_1)n''(z_1) \int_{-\infty}^{\infty} dz z^2 \int_{|z|}^\infty dr F(r)(r^2 - 3z^2).$$

We discard contributions from the 0 and $L$ boundaries in the $z_1$ integral, and perform the $z$ integral to obtain

$$\sigma = \frac{2\pi}{15} \int_0^\infty dr F(r)r^5 \int_{-\infty}^{\infty} d\zeta \left[n'(\zeta)\right]^2.$$  (83)

Thus we see that the microscopic theory leads to

$$\sigma = a \int_{-\infty}^{\infty} d\zeta \left[n'(\zeta)\right]^2 = \frac{A(n_1 - n_0)^2}{\lambda}$$  (84)
in the limit of slow density variation. This has the same form as that obtained from the van der Waals theory by Cahn and Hilliard [18] and Fisk and Widom [17], and also from a fluctuation theory by Triezenberg and Zwanzig [7]. According to Lovett et al. [8], the same form was obtained long ago by Ornstein and Zernike [19] with the coefficient \( a \) given by

\[
a = \frac{2\pi}{3} T \int_0^\infty dr \, c(r) \, r^4,
\]

where \( c(r) \) is the direct correlation function. This result is readily seen to be identical to (83) in the low-density limit

\[
g = \exp \left( -\frac{u}{T} \right), \quad \epsilon = \exp \left( -\frac{u}{r} \right) - 1.
\]

We now turn to the surface energy, which to our knowledge has only been considered for a step-function density variation [1]. Starting with (52) and proceeding as for \( \sigma \), we find

\[
\epsilon' = \pi \int_0^L dz_1 \, n(z_1) \int_0^L dz_2 \, n(z_2) \int_0^\infty dr \, h(r)
\]

\[
= \pi \int_0^L dz_1 \, n(z_1) \int_{-\infty}^L dz \, \left[ n(z_1) + \frac{1}{2} z^2 n''(z_1) + \cdots \right] \int_0^\infty dr \, h(r).
\]

Liquid–vapour interface contributions come only from \( z_1 \approx D \approx z_2 \), and since \( D \) and \( L-D \) are macroscopic distances, the integral over \( z \) may be taken from \( -\infty \) to \( +\infty \) when extracting the interface contributions. The first derivative gives a zero contribution, as before. The second derivative contributes to \( \epsilon \) by the amount

\[
-\frac{\pi}{3} \int_0^\infty dr \, h(r) r^3 \int_{-\infty}^\infty d\zeta \, \left[ n'(\zeta) \right]^2,
\]

which, like \( \sigma \), is proportional to \( (n_1 - n_v)^2/\lambda \). The dominant contribution for large \( \lambda \) is however not (87) but the liquid–vapour interface part of the first term in (86), i.e.

\[
2\pi \int_0^L dz_1 \, n^2(z_1) \int_0^\infty dr \, h(r) r.
\]

To extract the interface part of \( \int_0^L dz \, n^2(z) \), we write the density as

\[
n(z) = n_D(z) + (n_1 - n_v) \delta f(z),
\]

where

\[
n_D(z) = \begin{cases} n_1, & z < D, \\ n_v, & z > D. \end{cases}
\]

The constant parts \( n_1 \) and \( n_v \) of \( n(z) \) give bulk terms, while the mixed term

\[
2n_D(z)(n_1 - n_v) \delta f(z)
\]

contributes (to \( \int_0^L dz \, n^2(z) \)) by the amount

\[
2(n_1 - n_v) \left\{ n_1 \int_{-\infty}^0 d\zeta \, \delta f(\zeta) + n_v \int_0^\infty d\zeta \, \delta f(\zeta) \right\}.
\]
On using the convention (64) for the location of the dividing surface, this becomes

\[-2(n_1 - n_v)^2 \int_0^\infty d\zeta \tilde{\delta} f(\zeta)\].

The last term in \(\int_0^L dz \, n^3(z)\) is

\[(n_1 - n_v)^2 \int_{-\infty}^\infty d\zeta \tilde{\delta} f(\zeta)\]

so that the total interface contribution to (88) is

\[2\pi (n_1 - n_v)^2 \int_0^\infty dr \, h(r) r \left\{-2 \int_0^\infty d\zeta \tilde{\delta} f(\zeta) + \int_{-\infty}^\infty d\zeta \left[\tilde{\delta} f(\zeta)\right]^2\right\}. \tag{89}\]

When the surface is characterized by a single length \(\lambda\), both of the \(\zeta\) integrals are proportional to \(\lambda\); thus the dominant part of \(\epsilon\) for a slowly varying density is

\[\epsilon = B(n_1 - n_v)^2 \lambda. \tag{90}\]

This form is in agreement with the large \(\lambda\) limit obtained for the exponential density variation, equation (81), and the coefficient

\[B = -\frac{3\pi}{2} \int_0^\infty dr \, h(r) r \tag{91}\]

of (81) can be verified from the more general expression (89) with the substitution of (73) for \(\tilde{f}\).

6. THERMODYNAMIC CONSISTENCY

The thermodynamics of surfaces is discussed in general terms by Ono and Kondo [16]. They show that when the dividing surface is chosen according to (64) (the equimolecular dividing surface), the surface tension \(\sigma\), surface energy \(\epsilon\) and surface entropy \(s\) are related by

\[\sigma = \epsilon - T s, \quad s = \frac{d\sigma}{dT}, \tag{92}\]

in direct analogy to the relations in the bulk, namely

\[F = E - TS, \quad S = -\left(\frac{\partial E}{\partial T}\right)_V.\]

The two relations (92) imply

\[\epsilon = \sigma - T \frac{d\sigma}{dT} = -T^2 \frac{d}{dT} \left(\frac{\sigma}{T}\right). \tag{93}\]

In principle this equation together with the expressions for \(\sigma\) and \(\epsilon\) puts a constraint on the density variation. For example, it could be used to obtain the thermodynamically consistent \(\lambda\) by comparison of (77) and (78). Freeman and McDonald [14] were aware of this possibility, but did not have an expression for \(\epsilon\) available. Analytically this programme is too complicated except in limiting cases, which we will now examine.
Consider the $\lambda \to 0$ (step function) limit first. As explained in § 4, this limit does not give a satisfactory surface energy for the liquid–vapour interface. However, we can apply our theory to the interface between an infinitely steep wall and a dilute gas, for which we can use the low-density approximation (85) for $g$. The theory gives (cf. (79))

$$
\sigma_0 = \frac{\pi}{8} n_v^2 \int_0^\infty dr \, r^4 \exp \left( -\frac{u}{T} \right) \frac{du}{dr},
$$

$$
\epsilon_0 = -\frac{\pi}{2} n_v^2 \int_0^\infty dr \, r^3 \exp \left( -\frac{u}{T} \right) u.
$$

The expression for $\sigma_0$ gives, on integration by parts,

$$
\frac{\sigma_0}{T} = \frac{\pi}{2} n_v^2 \int_0^\infty dr \, r^3 \left( \exp \left( -\frac{u}{T} \right) - 1 \right),
$$

so that the relation

$$
-T^2 \frac{d}{dT} \left( \frac{\sigma_0}{T} \right) = \epsilon_0
$$

is exactly satisfied for a temperature change at constant volume (and thus constant density).

The consequence of thermodynamic consistency in the large $\lambda$ limit will be discussed in the next section.

7. CRITICAL EXPONENTS

As the critical point is approached, many physical quantities diverge or go to zero as $T_c - T$ to some exponent. If we write

$$
t = \frac{T_c - T}{T_c},
$$

then, in the notation of Widom [20],

$$
\sigma \sim t^\mu, \quad \lambda \sim t^\nu, \quad n_1 - n_v \sim t^\beta, \quad C_v \sim t^\alpha, \quad \chi_T \sim t^{-\gamma}.
$$

We will also define exponents for $\epsilon$ and the coefficients $A$ and $B$ in the relations (84) and (90):

$$
\epsilon \sim t^\mu, \quad A \sim t^\alpha, \quad B \sim t^\beta.
$$

The exponent $\mu'$ can be evaluated immediately from the thermodynamic relation (93):

$$
\mu' = \mu - 1.
$$

This relation may also be obtained by a simple extension of the physical argument of Widom ([20], p. 80), which shows that $\sigma/\lambda$ is the singular part of the free-energy density, and thus $\mu + \nu$ is linked to the specific heat exponent $\alpha$ by ([20], equation (3))

$$
\mu + \nu = 2 - \alpha.
$$

The same reasoning shows that $\epsilon/\lambda$ is that part of the bulk energy density which carries the specific heat singularity, so that

$$
\mu' + \nu = 1 - \alpha.
$$

Combining (98) and (99) we regain (97).
Turning to the exponents $\alpha'$ and $\beta'$, we see from (84) and (90) that these are given by

$$\mu = \alpha' + 2\beta + \nu$$  \hspace{1cm} (100)

and

$$\mu' = \beta' + 2\beta - \nu.$$  \hspace{1cm} (101)

Now if we assume the truth of the relations (3), (5) and (7) in Widom's review [20], we have (in three dimensions) the equalities

$$\mu + \nu = 2 - \alpha = 3\nu = \gamma + 2\beta.$$  \hspace{1cm} (102)

Using these in (100) we find for the exponent of $A$

$$\alpha' = \gamma - 2\nu$$  \hspace{1cm} (103)

which is the result obtained by Fisk and Widom [17]. For $\beta'$ we have, from (97), (101) and (102)

$$\beta' = \gamma - 1.$$  \hspace{1cm} (104)

With the approximate numerical values [20]

$$\gamma \approx 1.25, \quad \nu \approx 0.64$$

we have

$$\alpha' \approx -0.03, \quad \beta' \approx 0.25.$$

In our microscopic theory, the coefficients $A$ and $B$ are proportional to

$$\int_0^\infty dr \, r^5 \, g(r, \bar{n}) \frac{du}{dr}$$ and $$\int_0^\infty dr \, r^2 \, g(r, \bar{n}) u(r),$$

and it is hard to see how these could be singular when $u(r)$ is a short-ranged interaction potential. However, Rice and Chang [21] have pointed out that a similar difficulty exists with the bulk potential energy, which (above $T_c$) has the form of our $B$, and yet is singular, varying as $t^{1-\alpha}$. This leads to the question: why is $\beta'$ not equal to $1 - \alpha$? A possible answer is that $B$ is proportional to the potential energy of an unstable phase (for $T \gtrsim T_c$, $\bar{n}$ is in the unphysical region of the $n$, $T$ plane). Another possibility is that our microscopic expressions for the $A$ and $B$ coefficients are not complete, and that something slipped through the net when we made the approximation

$$n_2(r_1, r_2) = n(x_1)n(x_2)g(r_{12}, \bar{n}).$$

We conclude this section with some observations concerning the range of validity of the power laws (95). In § 4 we saw that the large $\lambda$ limit integrands for $\sigma$ and $\epsilon$ gave good agreement with the exact integrands for the exponential surface, even down to $\lambda = d$. This comparison was with $g = \exp(-u/T)$, which is not adequate near the triple point; however, the qualitative features of the integrands and the accuracy of the large $\lambda$ expressions are not expected to be different when a more accurate pair correlation function is used. Note that this increases the range of validity of the van der Waals theories (e.g. Fisk and Widom [17]) set up to operate in the critical region, which give the same form for $\sigma$ as our large $\lambda$ expression. It is known experimentally that $\sigma \sim t^n$ (see, for example, Zollweg et al. [22], Smith et al. [23]) and $(n_1 - n_c) \sim t^\eta$ (Stansfield [24]),
hold over a large temperature range and a recent theory of surface tension by Lovett et al. [8] has predicted that $\lambda \sim t^{-0.65}$ also holds far from the critical point. We expect the power laws to hold over the same temperature range in which the large $\lambda$ expressions

$$\sigma = A(n_1 - n_v)^2/\lambda, \quad \epsilon = B(n_1 - n_v)^2\lambda$$

are a good approximation, which appears to be all the way to the triple point. In terms of

$$\tau = \frac{T_c - T}{T_c - T_t}$$

this would imply that the relations

$$\sigma = \sigma_t \tau^\eta, \quad \epsilon = \epsilon_t \tau^{\eta - 1} \quad \text{and} \quad \lambda = \lambda_t \tau^{-\nu}$$

were valid all the way from $\tau = 0$ to $\tau = 1$. We will show in § 8 that the results of the large $\lambda$ limit do indeed give satisfactory values for $\lambda$ near the triple point.

### 8. THE SURFACE THICKNESS

We have shown that the large $\lambda$ limits are a good approximation when $\lambda$ is of order of the core diameter, and that the coefficient $B$ in the large $\lambda$ expression for $\epsilon$ is proportional to the bulk potential energy of a fluid at density $n$. These facts enable us to determine the surface thickness at the triple point. We proceed as follows: $\sigma$, $n_1 - n_v$ and the potential energy per molecule in the liquid

$$\frac{\langle U \rangle}{N} = 2\pi n_1 \int \delta dr r^2 g(r, n_1)u(r)$$

are all known from experiment, and $\epsilon$ can be deduced from the temperature variation of $\sigma$. From $\langle U \rangle$ we can obtain the value of our coefficient $B$ (given by (91)) at the triple point, on the assumption that $\pi \approx n_1$:

$$n_1 B = -\frac{3}{2} \frac{\langle U \rangle}{N}.$$  

Thus, from (90),

$$\lambda_t = \frac{\epsilon_t}{B(\Delta n)} \approx \frac{\epsilon_t}{B \rho_{1f} q},$$

i.e. $\lambda$ can be found directly from experimental data. The table gives the relevant parameters for Ar, Kr and Xe. We find an average value of $\lambda/d = 0.63$, with a maximum deviation of less than 4 per cent. This result is highly satisfactory when we remember that the surface thickness is approximately $2\lambda$, i.e. the surface thickness near the triple point comes out to be a bit larger than the core diameter $d$. It is also in accord with Egelstaff and Widom [25], who point out that the fundamental length $\chi_{t\sigma}$ is approximately equal to $0.07d$ at the triple point. Then, using a relation proposed by Mayer from the theory of the hard-sphere fluid [26] and approximating the hard-core diameter by $d$, they find that $\chi_{t\sigma} \approx 0.05d$. Thus Egelstaff and Widom have $\lambda/d \approx 0.7$ near the triple point, in excellent agreement with our results above. Finally, Lovett et al. [8] find similar values for surface thickness near the triple point comparing their direct
correlation function theory with experimental data for argon, although the value they extract from Toxvaerd [6] in their table 1 looks the best agreement with our results.

9. THE DIRECT CORRELATION-FUNCTION THEORY FOR $\sigma$

Alternative statistical mechanical expressions for the surface tension have been given by Yvon [29], Buff and Lovett [30], Triezenberg and Zwanzig [7] and most recently by Lovett et al. [8]. In these formulations the interatomic force does not appear explicitly, and correlations appear through the direct correlation function $c(r_1, r_2)$ rather than through the pair-correlation function $g(r_1, r_2)$. We shall use the techniques developed in this paper to reduce the direct correlation-function expression, and to obtain results which parallel those we obtained with the pair-correlation-function expression. Finally, we show that the two theories are equivalent in the lowest order in density.

Our starting point will be equation (11) of Lovett et al. [8]:

$$\sigma_0 = \frac{1}{2} \int \int d\bar{z} \frac{dn(\bar{z}_1)}{d\bar{z}_1} \frac{dn(\bar{z}_2)}{d\bar{z}_2} \int d\bar{y} \int d\bar{y}^2 c(r_{12}, z_1, z_2)(x_{12}^2 + y_{12}^2),$$  \hspace{1cm} (109)

which gives the surface tension of a plane liquid–vapour interface in the neighbourhood of $\bar{z}=0$. This expression may be reduced to a three-fold integral by the use of cylindrical polars (c.f. equation (25)):

$$\sigma_0 = \frac{\pi}{2} \int d\bar{z}_1 \frac{dn(\bar{z}_1)}{d\bar{z}_1} \int d\bar{z}_2 \frac{dn(\bar{z}_2)}{d\bar{z}_2} \int d\bar{y} \int d\bar{y}^2 \rho \left(\sqrt{\rho^2 + z_{12}^2}, z_1, z_2\right) \rho^2$$

$$= \frac{\pi}{2} \int d\bar{z}_1 \frac{dn(\bar{z}_1)}{d\bar{z}_1} \int d\bar{z}_2 \frac{dn(\bar{z}_2)}{d\bar{z}_2} \int d\bar{y} \int d\bar{y}^2 c(r, z_1, z_2)(r^2 - z_{12}^2).$$  \hspace{1cm} (110)

Equation (110) may be applied immediately to a step function density at $z=0$ (e.g. at the boundary of a single phase of density $n_v$ and an ideal wall). We find

$$\sigma_0 = \frac{\pi}{2} n_v \int d\bar{r} \bar{r}^2 c(r, 0, 0).$$  \hspace{1cm} (111)

In the dilute gas limit, this reduces to the result obtained in § 6.
We now give, with abbreviated discussion, results obtained with the approximation analogous to (32), namely
\[ c(r_{12}, z_{1}, z_{2}) \simeq c(r_{12}, \bar{n}). \]  
(112)

Interchanging the order of integration as in (49), we have from (110)
\[ \sigma_{c} = \frac{\pi}{2} T \int_{0}^{\infty} dr \: \rho c(r, \bar{n}) \int_{-\infty}^{\infty} dx_{1} \: \frac{dn(z_{1})}{dz_{1}} \int_{z_{1}-r}^{z_{1}+r} dx_{2} \: \frac{dn(z_{2})}{dz_{2}} (r^{2} - z_{12}^{2}). \]  
(113)

For the exponential density variation (71),
\[ \frac{dn}{dz} = -\frac{1}{2\lambda} (n_{1} - n_{2}) \exp \left( -\frac{|z|}{\lambda} \right) \]  
(114)

and we find (cf. § 4)
\[ \sigma_{c} = \frac{\pi}{2} T (n_{1} - n_{2})^{2} \int_{0}^{\infty} dr \: \rho c(r, \bar{n}) \]  
\[ \times \left\{ r^{2} - 4\lambda^{2} + \lambda^{2} \exp \left( -\frac{r}{\lambda} \right) \left( 4 + \frac{r^{2}}{\lambda^{2}} + \frac{r^{2}}{\lambda^{2}} \right) \right\}. \]  
(115)

The \( \lambda \to 0 \) limit checks with equation (111). If we put \( g = \exp \left( -u/T \right) \) in (77) and integrate by parts, we get (115) with \( c = \exp \left( -u/T \right) - 1 \). In the large \( \lambda \) limit we find
\[ \sigma_{c} = \frac{\pi}{6} T (n_{1} - n_{2})^{2} \frac{1}{\lambda} \int_{0}^{\infty} dr \: r^{4} c(r, \bar{n}), \]  
(116)

which is in agreement with (80) to the lowest order in density. The integrands in the full expression (115) for \( \sigma_{c} \), and in the limiting expressions for \( \lambda \to 0 \) and \( \lambda \to \infty \), are compared in figure 5 for \( c = \exp \left( -u/T \right) - 1 \) at \( \lambda = d \). We see that

![Figure 5](image-url)
the large $\lambda$ expression for $\sigma$ is a very good approximation even at $\lambda = d$, while $\sigma_0$ is much larger than $\sigma$. This is in agreement with figure 3 and the remark following equation (115).

Next we apply the gradient method of § 5. Integrating equation (113) by parts we obtain

$$\sigma_c = \pi T \int_0^\infty dr \, c(r, \bar{n}) \int_{-\infty}^{\infty} dz_1 n'(z_1) \int_{z_1 - r}^{z_1 + r} dz_2 \, z_2 n(z_2). \quad (117)$$

The last integral may be written as

$$\int_{z_1 - r}^{z_1 + r} dz_2 \, n'(z_2) = \int_{-r}^r dz \, n'(z) + \frac{1}{2} r^2 n''(z_1) + \ldots,$$

so that

$$\sigma_c = \frac{2\pi}{3} T \int_0^\infty dr \, r^4 c(r, \bar{n}) \int_{-\infty}^{\infty} dz \, [n'(z)]^2 \quad (118)$$

This result was stated by Lovett et al. (equations (12) and (13)) and credited to Ornstein and Zernike, and is the counterpart of equation (83). The equivalence of (116) and (118) for the particular case of the exponential density variation is easily verified.

We turn finally to the question of the equivalence or non-equivalence of the $g(r_1, r_2)$ and $c(r_1, r_2)$ theories. Lovett et al. refer to the two theories as 'complementary', and do not discuss their equivalence. But both theories are claimed to be general (except that the pair-correlation-function theory is usually restricted to pairwise interactions). Thus they are either rigorously equivalent, or at least one is approximate. Consider the general expression (110), transcribed to the geometry of figure 1. Integrate by parts twice, neglecting the contributions which do not come from the liquid–vapour interface. This gives

$$\sigma_c' = \frac{\pi}{2} T \int_0^L dz_1 \, n(z_1) \int_0^L dz_2 \, n(z_2) \frac{\partial^2}{\partial z_1 \partial z_2} \int_0^\infty dr \, c(r, z_1, z_2) (r^2 - z_{12}^2). \quad (119)$$

Comparison with

$$\sigma_g' = \frac{\pi}{2} \int_0^L dz_1 \, n(z_1) \int_0^L dz_2 \, n(z_2) \int_{|z_{12}|}^\infty dr \, g(r, z_1, z_2) \frac{du}{dr} (r^2 - 3z_{12}^2) \quad (25a)$$

shows that the two theories are equivalent for central pairwise interactions if

$$T \frac{\partial^2}{\partial z_1 \partial z_2} \int_{|z_{12}|}^\infty dr \, c(r, z_1, z_2) (r^2 - z_{12}^2) \int_{|z_{12}|}^\infty dr \, g(r, z_1, z_2) \frac{du}{dr} (r^2 - 3z_{12}^2). \quad (120)$$

A general proof of equivalence is thus seen to require knowledge of relationships between $c$, $g$ and $u$ for inhomogeneous systems. It is possible to show, however, that $\sigma_g$ and $\sigma_c$ are identical to the lowest order in density. Using the identity

$$\frac{\partial^2}{\partial z_1 \partial z_2} f(|z_{12}|) = -2 \delta(z_{12}) f'(|z_{12}|) - f''(|z_{12}|), \quad (121)$$
we find that the left side of (120) reduces to
\[
2T \left\{ \int_{|z|=1} \infty dr \, r c(r, \bar{n}) - z_{12}^2 c(|z_{12}|, \bar{n}) \right\}
\]
when \(c(r_1, r_2)\) is approximated as in (112). The right side of (120) is easily shown to be equal to this expression when we take \(g = \exp (-u/T)\) and \(c = \exp (-u/T) - 1\).

References