The Superficial Density of Matter at a Liquid-Vapor Boundary

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The distribution of matter within the transition layer between the two phases of a fluid system is considered. Approximate values are obtained for the superficial density of matter Γ, calculated with reference to the Gibbs surface of tension as the dividing surface between the phases.

I. INTRODUCTION

IN accordance with the Gibbs theory of capillarity as applied to the surface between a one-component liquid and its vapor, it is found that the surface tension σ at the boundary and the Gibbs potential μ for the fluid should be connected at constant temperature by the equation[1]

$$d\sigma = -\Gamma d\mu, \qquad (I.1)$$

where Γ is the so-called superficial density of matter at the boundary. This quantity Γ may be defined as the difference—per unit area of boundary surface—between the actual amount of fluid in the two-phase system and the amount which it would contain if the liquid and vapor phases retained uniform densities to the Gibbs surface of tension as the dividing surface between the phases.

In order to make actual applications of this important equation, it is necessary to have a value for the superficial density Γ at the liquid-vapor boundary in question. It is the purpose of the present article to calculate the values that can be expected for Γ in the case of typical fluid systems such as are commonly investigated in experiments on surface tension.

The calculations will involve certain assumptions and approximations which cannot be regarded as strictly correct. Nevertheless, it is believed that the treatment will be sufficiently sound to provide reliable results for the sign and order of magnitude of Γ. This is important for understanding the consequences of the Gibbs theory, since previously it has not even been clear whether the superficial density would have a positive or negative sign when referred to the

surface of tension. Application of the results obtained will be made in a subsequent article.

We may now proceed to the derivation of the desired relations. Since this proves to be a somewhat lengthy and involved task, we may begin by giving a brief outline of the sequence of treatment.

In the immediately following Section II, we shall use van der Waals' equation to investigate the values of fluid pressure and density to be expected in the transition layer between phases. We shall thereby be led to quantitative results needed in the subsequent development, as well as to the important qualitative conclusion that the density of the fluid γ can be expected, on passage through the layer from vapor to liquid, first to rise continuously from its value γ'' in the bulk of the vapor to a maximum value γ_{max} possible for vapor, then to rise abruptly to a minimum value γ_{min} possible for liquid, and then finally to rise again continuously to the value γ' which it has in the bulk of the liquid.

In Section III, we shall consider the condition of the fluid as a function of position within the transition layer, and shall introduce approximate expressions giving fluid pressure—first as a function of position as we pass through the vapor phase from the region of homogeneous vapor to the point of abrupt change in density and pressure—and then as a function of position as we pass from this point through the liquid phase to the region of homogeneous liquid.

In Section IV, we shall then substitute our expressions for fluid pressure as a function of position into two previously derived relations,[2] which give surface tension σ in terms of pressure distribution, and give a condition on the location of the surface of tension also in terms of pressure

[1] J. W. Gibbs, *Collected Works*, (Longmans Green and Company, New York, 1928), Vol. I, Eq. (508), p. 230.

[2] R. C. Tolman, J. Chem. Phys. **16**, 758 (1948).

distribution. The first of these substitutions will provide information as to the magnitudes of the parameters that appear in our selected expressions for pressure as a function of position, and the second substitution will allow us to fix the location of the surface of tension in the transition layer.

In Section V, we shall now have all that is necessary to calculate values of the superficial density Γ by evaluating the appropriate integrals for density differences as a function of position on the two sides of the surface of tension. The values found for Γ will, of course, depend on the nature and temperature of the fluid, but will, in general, be positive in typical cases.

Finally, in Section VI, we shall make some concluding remarks as to the extent of validity that can be expected for our results.

II. APPLICATION OF VAN DER WAALS' EQUATION

a. Introduction of the Equation

In order to investigate the distribution of fluid within the transition layer between a liquid and its vapor, we shall need to have a relation connecting the pressure of the fluid at the temperature of interest with the succession of fluid densities that would be encountered on passing through the transition layer from one phase to the other. To meet this need we shall make use of the familiar equation of van der Waals,

$$[p + (a/v^2)](v - b) = RT. \qquad (II.1)$$

It is appreciated that this equation does not give an exact representation of p, v, T relations for any actual fluid. Nevertheless, it appears to be the obvious equation to adopt for our purposes as a first approximation, and we shall comment briefly later in Section VI on the validity of its application.

For our use, it will be desirable to re-express Eq. (II.1) by considering its application to unit mass of fluid. Replacing the volume v by the reciprocal of the density of the fluid γ, and solving for pressure p, we can then evidently write

$$p = (\gamma r T / 1 - \gamma/\gamma_\infty) - a\gamma^2, \qquad (II.2)$$

where r is the gas constant per unit mass of the fluid, and a and $1/\gamma_\infty = b$ are the previous van der Waals' constants taken for unit mass.

TABLE I. Choice of parameters.

$a\gamma'/rT$	5	7	8	9	10	11	13	Chosen
γ'/γ_∞	0.8	0.8571	0.875	0.8889	0.9	0.9091	0.9231	See Eq. (II.10)
γ'/γ''	80.69	425.9	1013	2447	5988	14800	92530	See Eq. (II.11)

b. Conditions on Parameters

In applying van der Waals' Eq. (II.2) to our problem we shall want to select values, or a range of values, for the parameters in the equation that will correspond to the conditions that are encountered in usual surface tension measurements.

For the parameter r, which is the gas constant per unit mass of the fluid, we can, of course, immediately take

$$r = R/M, \qquad (II.3)$$

where R is the gas constant per mole and M the molecular weight of the fluid.

To obtain a first condition on the other two parameters a and γ_∞ we can make use of the circumstance that we are going to be concerned, at least for the present, with plane surfaces of separation between liquids and vapors at temperatures well below the boiling point. We can then take the pressures p' and p'' in the interior of the homogeneous parts of the liquid and vapor phases as equal and small,

$$p' = p'' = p_0 \approx 0, \qquad (II.4)$$

where p_0 is the ordinary vapor pressure of the liquid for a plane surface, and by the order zero we mean small compared with the large values that will be assumed by the quantities on the right-hand side of (II.2) on substitution of the large value γ' for the density of the liquid. As a consequence we see that we can then take

$$1/(1 - \gamma'/\gamma_\infty) = (a\gamma'/rT) \qquad (II.5)$$

as giving a closely approximate condition on the values of the parameters γ_∞ and a.

To obtain a second condition on the values of these parameters, we can write in accordance with a well-known thermodynamic consequence of van der Waals' equation, the relation

$$\int_{\gamma''}^{\gamma'} \left(\frac{\gamma r T}{1 - \gamma/\gamma_\infty} - a\gamma^2 \right) \frac{d\gamma}{\gamma^2} = \int_{\gamma''}^{\gamma'} p_0 \frac{d\gamma}{\gamma^2}, \qquad (II.6)$$

TABLE II. Limiting values of pressure and density.

$a\gamma'/rT$	5	7	8	9	10	11	13	Chosen
γ_{max}/γ'	0.123	0.083	0.071	0.062	0.055	0.050	0.042	See Eq. (II.13)
γ_{min}/γ'	0.811	0.823	0.829	0.835	0.840	0.845	0.853	See Eq. (II.13)
$p_{max}/\gamma'rT$	0.061	0.041	0.035	0.031	0.028	0.025	0.021	See Eq. (II.14)
$-p_{min}/\gamma'rT$	0.980	1.947	2.479	3.036	3.614	4.208	5.446	See Eq. (II.14)
$p_0/\gamma'rT$	$1.24\ 10^{-2}$	$2.35\ 10^{-3}$	$9.87\ 10^{-4}$	$4.09\ 10^{-4}$	$1.67\ 10^{-4}$	$6.76\ 10^{-5}$	$1.08\ 10^{-5}$	γ''/γ' from Table I

which equates two different expressions for the reversible isothermal work that would accompany the transformation of unit mass of vapor into liquid, in one case by passing through all the intermediate metastable and unstable equilibrium states, predicted by van der Waals' equation as having densities between that of the vapor γ'' and that of the liquid γ', and in the other case by carrying out a direct condensation at the vapor pressure $p' = p'' = p_0$. Performing the indicated integrations, we can then write

$$rT \log \frac{\gamma'(1-\gamma''/\gamma_\infty)}{\gamma''(1-\gamma'/\gamma_\infty)} - a(\gamma'-\gamma'') = \frac{p_0}{\gamma''} - \frac{p_0}{\gamma'}, \quad (II.7)$$

or, since we shall be interested in applying this result at temperatures where the vapor is sufficiently dilute, so that we can take

$$\gamma'' \ll \gamma' < \gamma_\infty, \quad \text{and} \quad p_0 = p'' = \gamma'' rT, \quad (II.8)$$

we can rewrite this in the approximate form

$$\log \frac{\gamma'}{\gamma''} = \log\left(1 - \frac{\gamma'}{\gamma_\infty}\right) + \frac{a\gamma'}{rT} + 1, \quad (II.9)$$

which gives us a second condition connecting the parameters γ_∞ and a.

Finally, by solving Eq. (II.5), and by substitution in Eq. (II.9), we can write

$$\gamma'/\gamma_\infty = 1 - (rT/a\gamma'), \quad (II.10)$$

and

$$\log(\gamma'/\gamma'') = 1 + (a\gamma'/rT) - \log(a\gamma'/rT), \quad (II.11)$$

as the equations which we shall wish to use in determining appropriate values for the parameters.

c. Choice of Parameters

The foregoing equations will now permit us to relate the dimensionless quantity $a\gamma'/rT$, containing the parameter a, both to the dimension-

less quantity γ'/γ_∞, containing the parameter γ_∞, and to the observed ratio γ'/γ'' between the densities of the fluid in liquid and vapor form. Taking a range of values for $a\gamma'/rT$ that will cover the desired range of applications, we have used Eqs. (II.10) and (II.11) to calculate the values of γ'/γ_∞ and γ'/γ'' given in Table I.

It will be noted from Table I that we have chosen a range of values for $a\gamma'/rT$ that corresponds to a wide range of possible values for the observed ratio γ'/γ'', between the densities, in liquid and vapor form, of fluids that we may wish to consider. As will be seen later in Section V, this will be sufficient to permit a wide variation in the substances and temperatures to which our results can be applied.

d. Limiting Values of Pressure and Density

We are now ready to use van der Waals' Eq. (II.2) to provide information as to the values of density and pressure that the fluid can be expected to assume as we pass through the transition layer from the homogeneous part of the vapor phase at density γ'' and pressure $p'' = p_0$ to the homogeneous part of the liquid phase at density γ' and, in the case of plane dividing surfaces, again at the pressure $p' = p'' = p_0$. For this purpose we may first consider the maximum and minimum values of pressure which are known to be predicted by van der Waals' equation for temperatures below critical.

Differentiating (II.2) with respect to γ, we have

$$\frac{dp}{d\gamma} = \frac{rT}{(1-\gamma/\gamma_\infty)^2} - 2a\gamma \quad (II.12)$$

for the rate of change of pressure with density. Setting this expression equal to zero, and rearranging so as to express the result in conveni-

ent form, we then obtain

$$\left(1 - \frac{\gamma'}{\gamma_\infty}\frac{\gamma}{\gamma'}\right)^2\frac{\gamma}{\gamma'} = \frac{1}{2}\frac{rT}{a\gamma'} \qquad \text{(II.13)}$$

as an equation which determines the values of density γ at which the pressure p passes through a maximum or minimum.

In accordance with its cubic form, this equation has three solutions for the value of γ at which p is an extremum. At temperatures below critical, the smallest of these values occurs at a point which we may label (γ_{max}, p_{max}) where the pressure passes through a maximum, the next value occurs at a point (γ_{min}, p_{min}) where the pressure passes through a minimum, and the third solution is not of physical interest since it occurs at a value of γ greater than γ_∞.

Substituting the numerical values of $a\gamma'/rT$ and γ'/γ_∞ given in Table I as covering the range of interest, we can obtain numerical solutions of (II.13) for the values of γ/γ' at which the maximum and minimum of pressure occur. And rewriting van der Waals' Eq. (II.2) in a form which is more convenient for our present purposes,

$$p = \gamma'rT\left\{\frac{\gamma/\gamma'}{1 - \frac{\gamma'}{\gamma_\infty}\frac{\gamma}{\gamma'}} - \frac{a\gamma'}{rT}\left(\frac{\gamma}{\gamma'}\right)^2\right\}, \qquad \text{(II.14)}$$

we can also calculate the values of $p/\gamma'rT$ at these points of maximum and minimum pressure. The results of the calculations are given in Table II, where we also include a final line giving values of $p_0/\gamma'rT$ where $p_0 = p' = p''$ is the vapor pressure.

It will be seen from Table II, for the range of values of $a\gamma'/rT$ considered, that the densities γ_{max} at the pressure maximum are small compared with the densities γ_{min} at the pressure minimum. It will also be seen that the vapor pressures p_0 are small compared with the maximum pressures p_{max}, and that these in turn are small compared with the negative pressures $-p_{min}$ at the pressure minimum. It will further be noted that the values of the ratios $\gamma_{max}/\gamma_{min}$, p_0/p_{max} and $p_{max}/-p_{min}$ decrease as we go to larger values of $a\gamma'/rT$. These findings will play a role in our later introduction of approximations.

It may be remarked in this connection that the value of $a\gamma'/rT$ will be greater than 7 in all but one of the applications which we shall make.

The determination of the points (γ_{max}, p_{max}) and (γ_{min}, p_{min}) is of importance in setting the upper limit for the stable and metastable states of vapor that can exist at densities less than γ_{max}, and the lower limit for the stable and metastable states of liquid that can exist at densities greater than γ_{min}. States of the fluid at densities between γ_{max} and γ_{min} would be highly unstable since increase in density would be accompanied by decrease in pressure. In this connection it is illuminating to think of p_{max} as the maximum pressure which the vapor can withstand without collapse, and $-p_{min}$ as the maximum tension which the liquid can withstand without rupture. Extended regions containing fluid at densities between γ_{max} and γ_{min} are not to be expected.

e. Sequence of Values of Density and Pressure in the Transition Layer

We can now use the results of the foregoing discussion to predict the sequence of values of fluid density that we might expect to encounter on passage through the transition layer from vapor to liquid. Because of the short range of molecular forces, the density of the vapor can be expected to remain substantially constant at the value $\gamma = \gamma''$ which it has in the bulk of the vapor, until we come very close to the liquid. Under the action of attraction from the "liquid face," it can then be expected to rise at a rapidly increasing rate until it reaches the value $\gamma = \gamma_{max}$ at the upper limit of metastable vapor states. At this point we have $d\gamma/dp = \infty$, and the density can be expected to rise abruptly—through the range of densities corresponding to unstable states—to the value $\gamma = \gamma_{min}$ at the lower limit of metastable liquid states. Beyond this point, the density can then again be expected to increase at a slowly diminishing rate until it reaches the substantially constant value $\gamma = \gamma'$ in the bulk of the liquid.

The foregoing picture for the sequence of density changes also implies a corresponding picture for the sequence of pressure changes, which will prove useful in the next section. In accordance with the relation between pressure and density given by van der Waals' equation,

we are led to conclude, on considering passage through the transition layer from vapor to liquid, that the fluid pressure will first rise at a continuously increasing rate from its value $p=p''$ $=p_0$ in the interior of the vapor to the maximum value $p=p_{max}$ possible for vapor, will then fall abruptly to the minimum value $p=p_{min}$ possible for liquid, and then finally will again rise at a continuously decreasing rate to its value $p=p'$ $=p_0$ in the interior of the liquid. We note the contrast to the unreversed rise in fluid density on passage from vapor to liquid.

III. CONDITION OF FLUID AS A FUNCTION OF POSITION IN THE TRANSITION LAYER

The preceding section has provided qualitative information as to the sequence of fluid conditions to be expected on passage through the transition layer but has not provided any quantitative expressions for the condition of the fluid as a definite function of position in the layer. To meet this need, in the absence of a complete theory of fluid distribution in the layer, we shall now introduce approximate expressions, having a rational form compatible with available knowledge, and containing adjustable parameters with values to be determined later.

In formulating the desired expressions for fluid condition as a function of position, it is expedient to specify the condition of the fluid at any point by its pressure p, rather than by its density γ, since the rate of change of density with position becomes very large compared with the rate of change of pressure with position in regions where $d\gamma/dp$ approaches infinity. Hence, let us now consider the pressure of the fluid p as a function of a variable y, which we introduce to designate distances along an axis normal to the dividing surface between phases, and which we take as increasing in the direction from vapor to liquid, with the value $y=0$ at the point of abrupt change in density and pressure.

As appropriate expressions for pressure as a function of position, we shall than take

$$p-p'' = (p_{max}-p'')e^{+y/\lambda_v}, \qquad \text{(III.1)}$$

as holding over the range of vapor states from $y=-\infty$ to the point $y=0$ where the abrupt change in density and pressure occurs, and shall take

$$p-p' = (p_{min}-p')e^{-y/\lambda_l}, \qquad \text{(III.2)}$$

as holding over the range of liquid states from $y=0$ to $y=\infty$. The quantities λ_v and λ_l in these expressions are parameters whose values will be later considered.

These expressions are consonant with the information that we do have as to the distribution of fluid in the transition layer, and appear to be the most reasonable three parameter approximations that we can introduce at this stage. In accordance with (III.1), as we pass from $y=-\infty$ to $y=0$, the pressure p will rise from its value p'' in the bulk of the vapor phase to its maximum possible value p_{max}, asymptotically as we leave the interior of the vapor, and at a continuously increasing rate as we approach the "liquid face" exerting its strong, short range, attractive forces. And in accordance with (III.2), as we pass from $y=0$ to $y=+\infty$, the pressure p will rise from the minimum value p_{min} possible for liquid states to the value p' in the bulk of the liquid phase, at a continuously decreasing rate which gives asymptotic approach to the final conditions in the interior of the liquid. In accordance with van der Waals' equation, these changes in pressure will be accompanied by corresponding changes in density, where it will be noted that $d\gamma/dy$ becomes positive infinite at $y=0$, in agreement with our original picture of the abrupt increase in density at that point.

IV. APPLICATION OF PREVIOUSLY DERIVED EXPRESSIONS FOR SURFACE TENSION AND FOR THE LOCATION OF THE SURFACE OF TENSION

We may now consider the application to our present problem of two already existing expressions, for the magnitude of surface tension and for the location of the surface of tension, which have been previously derived for a one-component, two-phase system by treating the fluid within the transition layer by usual thermodynamic methods. These expressions, which are specialized for the case of spherical surfaces of separation, are of the form[3]

$$\sigma = \int_{-a}^{0} (p'-p)(1+cx)^2 dx$$
$$+ \int_{0}^{b} (p''-p)(1-cx)^2 dx, \quad \text{(IV.1)}$$

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[3] See reference 2, Eqs. (12.6) and (12.7).

TABLE III. Factors for computation of Γ.

$a\gamma'/rT$	5	7	8	9	10	11	13	Chosen
A	0.908	0.910	0.922	0.929	0.931	0.934	0.940	See Eq. (V.8)
$B\times10^8$	1.114	0.5619	0.4772	0.3680	0.3097	0.2669	0.2075	See Eq. (V.9)
$C\times10^{-8}$	0.8977	1.780	2.236	2.717	3.229	3.747	4.819	See Eq. (V.10)
$\log_{10}\gamma'/\gamma''$	1.9068	2.6293	3.0056	3.3888	3.7773	4.1702	4.9663	See Table I

and

$$0 = \int_{-a}^{0} (p'-p)(1+cx)xdx$$

$$+ \int_{0}^{b} (p''-p)(1+cx)xdx, \quad (IV.2)$$

where p, p', and p'' have the same significance as in the foregoing, c is the curvature of the surface of tension, and the integrations are taken with respect to a variable x which designates distances normal to the surface of tension and which increases in the direction from liquid to vapor with the value $x=0$ at the surface of tension and the values $x=-a$ and $x=b$ at points where the fluid reaches conditions in substantial agreement with those for the contiguous homogeneous phase.

To make use of Eqs. (IV.1) and (IV.2) in the present connection, we shall wish to substitute the expressions for $(p-p'')$ and $(p-p')$ given by (III.1) and (III.2) in the preceding section. In doing so, we note that the variable x in (IV.1) and (IV.2) and the variable y, which we found convenient for setting up the expressions (III.1) and (III.2), are connected by the relation

$$x = y_t - y, \quad (IV.3)$$

where y_t gives the position of the surface of tension as measured from the point of abrupt rise in density in the direction from vapor to liquid. We further note that we can also take

$$c=0, \quad \text{and} \quad p'' \equiv p' = p_0, \quad (IV.4)$$

since we are now concerned with plane dividing surfaces, where we have zero curvature c and have internal pressures in the two phases equal to the ordinary vapor pressure p_0.

Making the suggested substitutions, and expressing the results in terms of integrals taken with respect to the variable y, it will be seen

that we can now obtain the expressions

$$\sigma = \int_{-\infty}^{0} (p_0 - p_{\max})e^{y/\lambda_v}dy$$

$$+ \int_{0}^{\infty} (p_0 - p_{\min})e^{-y/\lambda_l}dy, \quad (IV.5)$$

and

$$0 = \int_{-\infty}^{0} (p_0 - p_{\max})e^{y/\lambda_v}(y_t - y)dy$$

$$+ \int_{0}^{\infty} (p_0 - p_{\min})e^{-y/\lambda_l}(y_t - y)dy. \quad (IV.6)$$

Performing the indicated integrations, we then find, as expressions for surface tension and for the location of the surface of tension,

$$\sigma = (p_0 - p_{\max})\lambda_v + (p_0 - p_{\min})\lambda_l, \quad (IV.7)$$

and

$$y_t = \frac{-(p_0 - p_{\max})\lambda_v^2 + (p_0 - p_{\min})\lambda_l^2}{(p_0 - p_{\max})\lambda_v + (p_0 - p_{\min})\lambda_l}. \quad (IV.8)$$

In order to make use of these equations, we may now introduce some approximations. In accordance with our discussion of the figures given in Table II, we can take

$$p_0 \ll p_{\max}, \quad p_0 \ll |p_{\min}|, \quad p_{\max} \ll |p_{\min}|. \quad (IV.9)$$

Furthermore, in accordance with the form of our expressions (III.1) and (III.2) and in accordance with the short range of molecular forces, it would seem reasonable to take

$$\lambda_v \approx \quad \text{or} \quad < \lambda_l, \quad (IV.10)$$

since we can expect the rise in the pressure of the vapor from p'' to $p_{\max}$ to be sharply concentrated as we approach the "liquid face," and the rise in pressure of the liquid from $p_{\min}$ to p' to take place as the result of increasing liquid density. Accepting these relations, we then see that Eqs. (IV.7) and (IV.8) would reduce to the

simplified approximate forms

$$\sigma = -p_{\min}\lambda_l \quad \text{and} \quad y_t = \lambda_l. \quad (IV.11)$$

Dropping the subscript of λ_l, and noting the approximations that can be introduced in (III.2), we may now write, as the expressions which we shall need in the next section,

$$\lambda = \frac{-\sigma}{p_{\min}}, \quad y_t = \lambda, \quad \text{and}$$

$$p = p_{\min}e^{-y/\lambda} \quad (0 < y < \infty), \quad (IV.12)$$

where the first of these relations will permit us to determine λ from experimental values of σ and calculated values of $p_{\min}$, the second relation will then give us the location of the surface of tension as measured from the point of abrupt rise in density at $y = 0$, and the third relation will give us the fluid pressure for the range of liquid states beyond that point.

V. CALCULATION OF SUPERFICIAL DENSITY

a. Deduction of Relations

We now have all that is needed to undertake the determination of superficial density Γ. In accordance with the definition of that quantity, it is evident that we can write

$$\Gamma = \int_{-\infty}^{y_t} (\gamma - \gamma'')dy + \int_{y_t}^{\infty} (\gamma - \gamma')dy, \quad (V.1)$$

where we integrate the excess density above that for homogeneous vapor up to the surface of tension, and integrate the excess density above that for homogeneous liquid from that point on—the first of the integrals being actually positive in value and the second negative. In view of the small value of γ'' and of the small values of γ until we reach the point $y = 0$ (see

TABLE IV. Values of superficial density Γ at 20°C.

Sub-stance	M g	σ dyne/cm	γ' g/cm³	γ'' ⊽ 10⁻⁵g/cm³	Γ 10⁻⁸g/ cm² ▮ 10⁻⁸ cm	$\Gamma/(\gamma'-\gamma'')$ 10⁻⁸ cm	$(M/N_0\gamma')^{\frac{1}{3}}$ 10⁻⁸ cm
Water	18.016	72.75	0.9982	1.73	0.98	0.99	3.11
Methyl alcohol	32.04	22.61	0.7915	16.95	0.80	1.01	4.07
Ethyl alcohol	46.07	22.27	0.7894	11.1	1.05	1.33	4.59
Acetic acid	60.05	27.63	1.0491	7.64	1.53	1.46	4.56
Ethyl ether	74.12	16.96	0.7135	187.0	2.49	3.50	5.57

Tables I and II), we shall now approximate this expression by

$$\Gamma = \int_0^{\lambda} \gamma dy + \int_{\lambda}^{\infty} (\gamma - \gamma')dy$$

$$= \lambda\gamma' + \int_0^{\infty} (\gamma - \gamma')dy$$

$$= \lambda\gamma' - \gamma' \int_0^{\infty} \left(1 - \frac{\gamma}{\gamma'}\right)dy, \quad (V.2)$$

where we have substituted $y_t = \lambda$ in accordance with (IV.12).

In order to re-express the integral in this equation in a form which can be evaluated, we note by equating the expressions for pressure given by (II.15) and (IV.2) that we can write

$$p_{\min}e^{-y/\lambda} = \gamma' rT \left\{ \frac{\gamma/\gamma'}{1 - (\gamma'/\gamma_\infty)(\gamma/\gamma')} - \frac{a\gamma'}{rT}\left(\frac{\gamma}{\gamma'}\right)^2 \right\}, \quad (V.3)$$

as a valid relation over the range of values of y from zero to infinity and over the corresponding range of values of γ/γ' from $\gamma_{\min}/\gamma'$ to unity. Introducing into (V.3) the convenient abbreviations

$$\frac{\gamma}{\gamma'} = z, \quad \frac{\gamma'}{\gamma_\infty} = g \quad \text{and} \quad \frac{a\gamma'}{rT} = \frac{1}{1-g} \quad (\text{cf. II.5}) \quad (V.4)$$

and then differentiating with respect to y and z, we can now obtain

$$dy = -\lambda\left\{\frac{1}{z} + \frac{g}{1-gz} - \frac{1-2gz}{(1-z)(1-g-gz)}\right\}dz, \quad (V.5)$$

as an expression for dy in terms of z and dz. Substituting in (V.2), we may then write our expression for Γ in a form

$$\Gamma = \lambda\gamma'\left\{1 + \int_{z=\gamma_{\min}/\gamma'}^{z=1}\left[\frac{1}{z} - 1 + \frac{g}{1-gz} - \frac{gz}{1-gz} - \frac{1}{1-g-gz} + \frac{2gz}{1-g-gz}\right]dz\right\}, \quad (V.6)$$

where the integral can be readily evaluated.

Performing the integration indicated in (V.6) , and substituting the limits given, we then obtain

$$
\Gamma = \lambda\gamma' \left\{ 2\frac{\gamma_{\min}}{\gamma'} - 1 + \log\frac{\gamma'}{\gamma_{\min}} \right.
$$

$$
-\left(\frac{\gamma_\infty}{\gamma'}-1\right)\log\left(\frac{\gamma_\infty}{\gamma'}-\frac{\gamma_{\min}}{\gamma'}\Big/\frac{\gamma_\infty}{\gamma'}-1\right)
$$

$$
\left. +\left(2-\frac{\gamma_\infty}{\gamma'}\right)\log\frac{2-\dfrac{\gamma_\infty}{\gamma'}}{1+\dfrac{\gamma_{\min}}{\gamma'}-\dfrac{\gamma_\infty}{\gamma'}} \right\}, \quad (V.7)
$$

as our desired expression for superficial density Γ referred to the Gibbs surface of tension. This expression permits us to compute specific values for Γ in terms of quantities that can be either directly measured or computed from appropriate values of van der Waals' constants. For the purpose of such computations the expression can be put into somewhat more usable forms.

Designating the sum of terms within the parentheses in (V.7) by the letter A, we can write

$$\Gamma = A\lambda\gamma', \quad (V.8)$$

where A is a numerical factor that can be computed from appropriate values for $\gamma_{\min}/\gamma'$ and γ'/γ_∞. Using the values of these quantities that are given in Tables I and II as corresponding to our selected range of values for $a\gamma'/rT$, we calculate for A the values given in the second line of Table III, where the nearly constant value for the factor A over a wide range of fluid conditions will be noted.

Furthermore, substituting into (V.8) the value of λ in terms of surface tension σ and of minimum pressure $p_{\min}$ as given by (IV.12), we can also write our expression for superficial density in the form

$$\Gamma = \frac{A\sigma\gamma'}{|p_{\min}|} = \frac{A\sigma M}{RT|p_{\min}|/\gamma'rT} = B\frac{\sigma M}{T}, \quad (V.9)$$

where T and M are the temperature and molecular weight of the fluid considered, and B is a

TABLE V. Superficial density of water 10°–50°C.

Temperature °C	σ dyne/cm	γ' g/cm³	γ'' 10^{-5} g/cm³	Γ 10^{-8} g/cm²	$\Gamma/(\gamma'-\gamma'')$ 10^{-8} cm	$(M/N_0\gamma')^{\frac{1}{3}}$ 10^{-8} cm
10	74.22	0.9997	0.941	0.96	0.96	3.11
20	72.75	0.9982	1.73	0.98	0.99	3.11
30	71.18	0.9957	3.035	1.00	1.01	3.11
40	69.56	0.9922	5.11	1.02	1.03	3.11
50	67.91	0.9881	8.32	1.05	1.06	3.12

factor which can be computed from the value of the gas constant per mole R, and from the values of A and of the ratio $|p_{\min}|/\gamma'rT$ as already given in Tables II and III. The calculated values of B corresponding to different values of $a\gamma'/rT$ are given in the third line of Table III.

Finally, we shall also find it useful to introduce the reciprocal of B and rewrite our expression for superficial density in the form

$$\Gamma = (1/C')(\sigma M/T), \quad (V.10)$$

where $C=1/B$. This is a convenient form for application to observational data, since the computed values of C are found to increase nearly linearly with computed values for $\log\gamma'/\gamma''$, where the densities γ' and γ'' of the fluid in liquid and vapor form are quantities subject to direct experimental determination. The calculated values for C and for $\log_{10}\gamma'/\gamma''$, which correspond to our selected range of values for $a\gamma'/rT$, are given in the last two lines of Table III, where interpolation is facilitated by the approximately linear relation between the two sets of quantities.

b. Application to Observational Data

With the help of Eq. (V.10) and the values for C and $\log_{10}\gamma'/\gamma''$ given in the last two lines of Table III, we may now compute numerical values for superficial density Γ for two-phase fluid systems from given values of the surface tension σ at the boundary, of the molecular weight M and temperature T of the fluid, and of the densities of the fluid γ' and γ'' in the liquid and in the vapor phase. We have made such computations for several different fluids at the same temperature (20°), and for a single fluid (water) at different temperatures.

The data and results for five different fluids at 20°C are given in Table IV. The substances

considered are given in the first column in the order of increasing molecular weights, and the molecular weights M are given in the second column. Values of the surface tension σ at 20°C are given in the third column.[4] The values for the densities γ' of the liquid and γ'' of the vapor at 20°C are given in the fourth and fifth columns.[5] And the desired values for the superficial density Γ at the Gibbs surface of tension are then given in the sixth column, as calculated from Eq. (V.10) with the help of the last two lines in Table III.

In addition to Γ, two other quantities which are given in the two final columns of the table will be of interest. The first of these quantities, $\Gamma/(\gamma'-\gamma'')$, will be seen from the definition of Γ as provided by Eq. (V.1) to give the distance, measured in the direction vapor to liquid, from a dividing surface located so as to make the superficial density vanish to the surface of tension with respect to which the superficial density has the value Γ. The second of the quantities, $(M/N_0\gamma')^{\frac{1}{3}}$, where N_0 is Avogadro's number, will be seen to give a measure of the distance between molecules of the liquid, treating them as points located in a cubical array.

The data and results for water at a series of temperatures from 10° to 50°C will be found in Table V. The sources of the data are the same as those already mentioned for the case of water in connection with the preceding table.

From Table IV, it would be concluded, for the liquid-vapor systems considered at 20°C, that the superficial density of matter Γ referred to the surface of tension is a positive quantity of the order of 0.8 to 2.5×10^{-8} g/cm², and that the

distance $\Gamma/(\gamma'-\gamma'')$ from a dividing surface located so as to make the superficial density vanish to the surface of tension is of the order of 0.25 to 0.6 of intermolecular distances $(M/N_0\gamma')^{\frac{1}{3}}$ in the liquid.

From Table V, it would be concluded that the superficial density Γ and the ratio of the distances $\Gamma/(\gamma'-\gamma'')$ to $(M/N_0\gamma')^{\frac{1}{3}}$ would be subject to a slight increase with temperature for a given liquid. This finding, together with the internal evidence in Table IV, would indicate that more concordant results would be found for different liquids if we could compare them at corresponding temperatures.

In connection with the foregoing results, it may be remarked that we could also have calculated values for the parameter λ, which determines the rate of exponential rise in the pressure of the liquid as we proceed from the value $p_{\min}$ at the point of abrupt change to the value p_0 in the interior of the liquid phase. Rewriting Eq. (V.8) in the form

$$\lambda = \Gamma/A\gamma', \qquad (V.11)$$

we see, in accordance with the values of A in Table III and with the relation $\gamma'' \ll \gamma'$, that the values of λ would be 6 to 10 percent greater than the values given in the next to the last columns of Tables IV and V. Hence the distance $\lambda = y_t$ from the point of abrupt rise in density to the surface of tension will be of the order of magnitude of intermolecular distances in the liquid.

VI. CONCLUDING REMARKS

In forming a judgment as to the degree of reliance to be placed on the foregoing results, we must begin by criticizing the general character of a method of investigation which treats microscopic distributions of matter by considerations primarily justified by their successful application to macroscopic distributions. In studying the behavior of matter in the transition layer between phases, we have treated it as a fluid which obeys a macroscopic equation of state (van der Waals' equation), and we have applied equations to its distribution (IV.1 and IV.2) which were themselves previously derived by the use of familiar macroscopic thermodynamic principles. It is evident from the outcome of the

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[4] The values for surface tension σ are taken from the *International Critical Tables*, (McGraw-Hill Book Company, Inc., New York, 1948), Vol. IV, pp. 447, 448, 449, and 451. Although our treatment is concerned with liquids in contact solely with vapor, we have actually taken values of σ for liquids in contact with air as well as vapor. We have done this to obtain a consistent set of values including cases where measurements in the absence of air are not available. The small decreases in σ resulting from the presence of air cannot be expected to have an important effect on our final figures.

[5] The values for the densities γ' and γ'' for water are taken from the *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1946), thirtieth edition. See p. 1695 and p. 1876 ff. The values of γ' and γ'' for the other liquids are from the results of Young as given in the tables of Landolt and Börnstein (Verlag Julius Springer, Berlin, 1923), fifth edition, Vol. I, Tables 79, 79d, 79g.

work itself, however, that the distribution of matter within the layer must change markedly within distances of the order of those between molecules. Hence the extent of the validity of our macroscopic modes of procedure is not clear. In justification for such a procedure, in agreement with our previous more extended discussion of the problem,[6] we can express the expectation, or at least the hope, that a more rigorous statistical mechanical treatment would lead to approximately similar results. And in extenuation for our procedure, we may emphasize the importance of doing the best we can at the present time to obtain information as to the sign and order of magnitude of the important quantity Γ.

Coming to more specific questions, we may next inquire into the validity of our use of van der Waals' equation as the equation of state for our fluid. In this connection it is to be emphasized that our method of selecting parameters for the equation is such as to secure values of γ' and γ'' which agree with the empirical densities of liquid and vapor at each actual temperature of interest. This avoids the serious errors that might otherwise arise from the known strong dependence of van der Waals' constant a on temperature. It may also be emphasized that we only need reliable results from the equation over a limited range of states. Nevertheless, it is not clear that van der Waals' equation with the adopted choice of parameters will give us a very accurate representation of the metastable liquid states that lie in the important range between (γ_{min}, p_{min}) and (γ', p'). We can perhaps be justified, however, in assuming that the equation does provide a correct qualitative picture of the succession of fluid states in the transition layer, and provides quantitative results of the correct order of magnitude.

We may next inquire into the validity of assuming exponential expressions of the form (III.1) and (III.2) to represent pressure as a function of position in the layer. In this con-

nection we may again emphasize the rational character of these expressions, which was discussed in more detail in Section III, and may also emphasize the circumstance that the quantities λ_v and λ_l are treated as adjustable parameters with values left open for later determination in Section IV. It will also be appreciated that our final results will be primarily dependent on the values found for γ_{min} and p_{min} and will not be very sensitive to the exact way in which density and pressure rise from these values to their final values γ' and p' in the interior of the liquid. Indeed, if we make the extreme assumption that γ and p both rise linearly in a distance l from their initial to their final values, we calculate values for Γ of the same order of magnitude as those to which we have actually been led.

To complete this inquiry into validity, we must also consider the various simplifications which have been introduced in the course of the deductions. These, however, all appear to be based on approximations which are justified by the relative magnitudes of the quantities involved.

In the light of the foregoing discussion, we are led to the tentative conclusion that our method of treatment has provided a qualitatively correct picture of the transition layer between a liquid and its vapor, has demonstrated that the superficial density of matter Γ referred to the surface of tension in our layer would be a positive quantity in cases of common interest, and has provided values for Γ which are of the correct order of magnitude. This conclusion is reinforced by the general internal consistency of our picture as made evident in the course of the treatment. It is also reinforced by the reasonable character of our specific finding (see V.11) that the distances λ—from the surface where the abrupt rise in density takes place to the surface of tension where changes in curvature alone do not require work—would be of the order of magnitude of those between molecules. Our findings will be employed in a proposed later application.

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[6] See reference 2—discussion in Section 16.