

The Surface Tension of Liquid Metals

Adam S. Skapski

Citation: *J. Chem. Phys.* **16**, 389 (1948); doi: 10.1063/1.1746898

View online: <http://dx.doi.org/10.1063/1.1746898>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v16/i4>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

**SHARPEN YOUR
COMPUTATIONAL
SKILLS.**



Subscribe for
\$49 | year



computing
in **SCIENCE & ENGINEERING**

Scientific
Computing
with GPUs

Neither the extreme assumption of sharp discontinuity, involved in (4), nor the extreme assumption of the equivalence of all sites, involved in (4a), can be expected to hold strictly; but if the general approach is right, the measured values of $d\sigma/dT$ should lie somewhere between those calculated from (4) and those calculated from (4a);

$$-[\Delta S_{\text{osc}}/A] < [d\sigma/dT] < -[(\Delta S_{\text{osc}} + \Delta S_{\text{cont}})/A]. \quad (7)$$

Those limiting values are tabulated in Table I for some liquid metals, together with the experimental figures. Under $(\Delta S_{\text{osc}} + \frac{1}{2}\Delta S_{\text{cont}})/A$ the mean values of the intervals are given for better orientation. The influence of the thermal expansion is expressed by the change of A with temperature. The calculations refer to the melt-

ing points with the exception of mercury where 20° was taken instead.

The experimental data lie well within the calculated interval and, as a matter of fact, almost coincide with the respective middle (average) values.

References

- (1) J. Frenkel, J. Phys. U.S.S.R. **3**, 350 (1940).
- (2) J. Frenkel and A. Gubanov, J. Exper. Theor. Phys. U.S.S.R. **16**, 435 (1946). See also A. Gubanov, J. Exper. Theor. Phys. U.S.S.R. **16**, 416 (1946).
- (3) H. Dupré, Ann. Chim. Phys. (4), **11**, 200 (1867).
- (4) A. Einstein, Ann. d. Physik (4), **4**, 513 (1901).
- (5) E. Madelung, Physik. Zeit. **14**, 729 (1913).
- (6) Compare, e.g., P. P. Ewald and C. Hermann *Strukturberichte*, Vol. I, p. 11.
- (7) Compare, e.g., N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1939), p. 6.

The Surface Tension of Liquid Metals

ADAM S. SKAPSKI

Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received December 24, 1947)

The author is opposed to the generally established opinion that the surface tension of liquid metals is abnormally high (as compared with that of non-metallic liquids) and that the metallic character (the presence of free electrons) is the main cause of the "high" surface tension of metals. He shows that this opinion is due to the fact that specific surface tensions (ergs per cm²) are compared and that the influence of temperature is not accounted for. Total surface energies $\sigma_M - T(d\sigma_M/dT)$ —where $\sigma_M = \sigma_{\text{sp}} \times A$ is the surface tension referred to the surface A occupied (in monomolecular layer) by N -Avogadro's molecules—are of the same order of magnitude.

The author expresses the opinion that the main cause of the surface tension of all liquids, whether metallic or not, is the same, *viz.*, the total surface energy is determined by

the amount of energy required to bring the molecules or atoms (and electrons) from the bulk of the liquid to its free surface while enlarging the surface area. He shows that in organic liquids showing no dipoles this energy can be calculated directly from the heat of vaporization at absolute zero and from the configuration of nearest neighbors. In the case of metals, the change of kinetic energy of electrons must be considered in addition. The author shows that the latter must contribute a negative term to the total surface energy. In fact, liquid metals show lower surface energies than might be expected from their heats of vaporization and from the configuration of their nearest neighbors (Fig. 1).

A short review of the recent electron theories of the surface tension of liquid metals is given.

THE opinion that the surface tensions of liquid metals are many times higher than those of non-metallic liquids has been generally accepted; consequently the belief that the metallic character (the presence of free electrons) is the main cause of the high surface tension of liquid metals has been the starting point for all modern electron theories of the surface tension

of metals. The present author thinks that the above opinion may well be due to a misinterpretation of the experimental data.

It is true that the surface tension of liquid silver (930 erg/sq.cm at m.p.) is about thirty times greater—and that of sodium (220 erg/sq.cm at m.p.) about eight times greater—than the surface tension of benzene (30 erg/sq.cm at

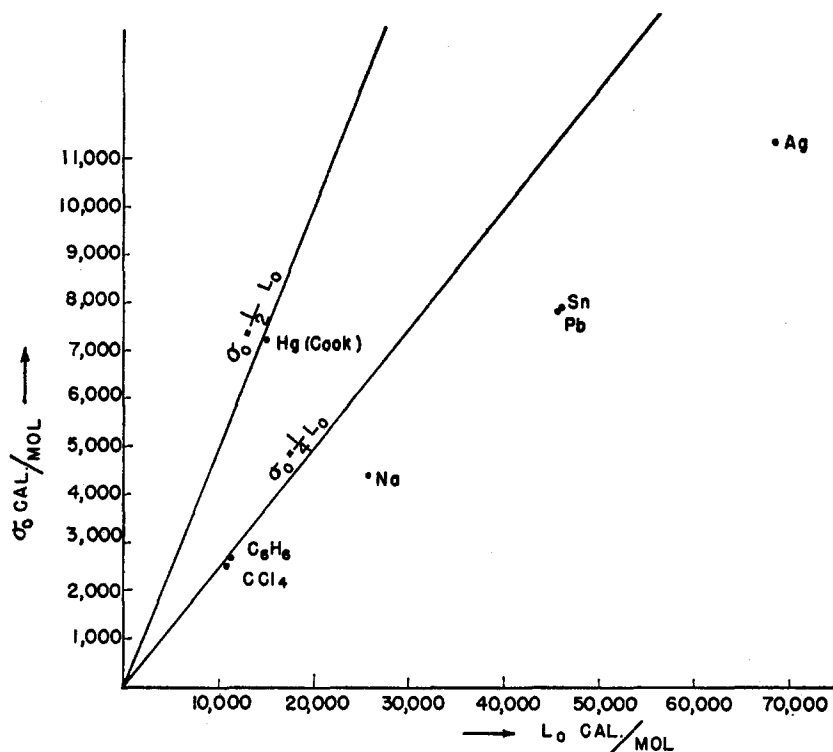


FIG. 1.

m.p.), but to compare the specific values (per square cm) is not fair. What we actually should compare are the molar surface tensions, i.e., the values referred to a surface occupied (in monomolecular layer) by N -Avogadro's molecules (or atoms). Such a surface A is given by

$$A = f \cdot N^{\frac{1}{3}} \cdot \left(\frac{M}{d} \right)^{\frac{2}{3}}, \quad (1)$$

where M is the molecular (or atomic) weight, d is the density of the liquid, and f is the factor accounting for the configuration or the packing of the liquid.

The arrangement in the surface layer of a liquid must correspond to that in the most densely populated plane of the respective configuration, because only such an arrangement assures the minimum of the free surface (and, of course, of free energy). The factor f is inversely proportional to the density of population in this surface arrangement and its value is: for close-packed liquids $f=1.09$, for body-centered cubic liquids (coordination number 8) $f=1.12$, for liquid mercury (coordination number 6) $f=1.04$.

The molar surface tension is defined by

$$\sigma_M = A \cdot \sigma_{\text{spec}}. \quad (2)$$

Furthermore, the surface tension varies with temperature, and its temperature coefficient $d\sigma_M/dT$, negative and usually constant, is appreciably greater for non-metallic, so-called "normal," liquids than for metals. To account for this we ought to compare, not the surface tensions as such, but the values of $[\sigma_M - T(d\sigma_M/dT)]$, the latter being practically independent of temperature, and, as may be easily seen, equal to the surface tension extrapolated to 0°K . The expression $\sigma_M - T(d\sigma_M/dT)$ is sometimes called "the total surface energy;" we shall denote it by σ_0 and, for the sake of convenience, express it in calories per molar surface A .

If we now substitute into $\sigma_M - T(d\sigma_M/dT)$ the experimental figures for σ_M and $d\sigma_M/dT$ we obtain the following ratio of the total surface energies (Table I):

TABLE I.

Liquid	σ_{spec} ergs/cm ²	$\frac{\sigma_{\text{spec}}}{\sigma_{\text{spec benzene}}}$	σ_0 cal./mole	$\frac{\sigma_0}{\sigma_0 \text{ benzene}}$
Benzene	30*	1	2650**	1
Na	220	7.5	4400	1.6
Pb	460	15	7770	2.8
Ag	930	31	11300	4

* All values at m.p.

** The values $\sigma_M - T(d\sigma_M/dT)$ were obtained by plotting $\sigma_M = \sigma_{\text{sp.}} A$ against T and determining the $d\sigma_M/dT$ from the slope.

We see that, if the surface energies of benzene, sodium, and silver are compared in this way, there is no drastic difference in the order of their magnitude.

We arrive at a still more striking result if we consider the relation between the surface energies of metallic and non-metallic liquids and their respective heats of vaporization.

The surface energy σ_0 of a normal, non-metallic liquid (showing no dipoles) can be rather accurately predicted from the heat of vaporization at 0°K and from the number of the nearest neighbors in the following way.

If we enlarge the surface of a liquid by A we have to bring N molecules (atoms) out of the bulk of the liquid and into the surface. The energy ΔU required for this purpose may be expressed in terms of surface tension (free energy) as follows:

$$\Delta U = \sigma_M - T(d\sigma_M/dT). \quad (3)$$

The energy ΔU may also be interpreted, however, as the difference of the potential energy of the molecules in the bulk and in the surface of the liquid. In the bulk each molecule is surrounded by Z_i nearest neighbors, while on the surface the number of its neighbors is smaller, viz., Z_a . If u is the energy of interaction between one pair of molecules, i.e., the work necessary to separate them to infinite distance, the difference of potential energy connected with bringing a molecule from the bulk to the surface will be

$$\Delta U = \frac{1}{2}Z_i u - \frac{1}{2}Z_a u. \quad (4)$$

Here, in the first approximation, u is supposed to be the same in the bulk and in the surface.

Now L_0 , the heat of vaporization at absolute zero, can be defined as

$$L_0 = \frac{1}{2}Z_i u$$

if we neglect the zero point energy. Hence it is possible to express u in terms of the heat of vaporization, namely,

$$u = \frac{2L_0}{Z_i}. \quad (5)$$

From (3), (4), and (5) we obtain

$$\left(\sigma_M - T \frac{d\sigma_M}{dT} \right) = \frac{Z_i - Z_a}{Z_i} L_0. \quad (6)$$

In close packed liquids $Z_i = 12$. As for Z_a , it must be equal to 9 because it must correspond to the most densely populated cross section plane through the configuration (to ensure the minimum of free surface and of free energy). Hence, for close-packed (or face-centered cubic) liquids we should expect

$$\sigma_M - T(d\sigma_M/dT) = \frac{1}{4}L_0. \quad (6a)$$

Formula (6a) should hold also for body-centered cubic liquids because of $Z_i = 8$ and $Z_a = 6$.

In Fig. 1, the $\sigma_M - T(d\sigma_M/dT)$ values of benzene and carbon tetrachloride, calculated from the experimental data, have been plotted against their respective heats of vaporization at 0°K. We see that the points fall practically on the line I drawn for the theoretical slope $\sigma_M - T(d\sigma_M/dT) = \frac{1}{4}L_0$. In the same Fig. 1, the $\sigma_M - T(d\sigma_M/dT)$ values of some metals have been plotted against their respective L_0 values.

It is evident from Fig. 1, that the $\sigma_M - T(d\sigma_M/dT)$ values of liquid metals all lie *below* the line I , i.e., that liquid metals show *smaller* surface energies than might be expected from their heats of vaporization and from the number of their nearest neighbors.

As for mercury (line II), it has six nearest neighbors in the liquid as well as in the solid state; hence, assuming the same symmetry of configuration as it has in the solid state, we arrive at $Z_i = 6$ and $Z_a = 3$, and, consequently, at $\sigma_M - T(d\sigma_M/dT) = \frac{1}{2}L_0$. The experimental $\sigma_M - T(d\sigma_M/dT)$ value falls practically on the theoretically expected line II with no greater deviation than it is the case of benzene and carbon tetrachloride. Mercury thus seems to behave like a non-metallic liquid, as far as its surface tension is concerned.

Thus, whether we accept the proposed theoretical relation between $\sigma_M - T(d\sigma_M/dT)$ and L_0 , or regard it as an empirical one, we have to admit that the metallic character of a liquid contributes a *negative term* to its surface energy rather than being its main cause.

With respect to the last conclusion, it may be of interest to notice a characteristic point common to all electron theories of surface tension of metals. Each author invariably points out that the theories precedent to his own should lead to *negative* values for the surface tension, and

claims that positive values previously obtained were due either to an error or to some unjustified assumptions.

Let us illustrate this point in a short review. The first electron theory of the surface tension was proposed by Gogate and Kothari.¹ They treat the surface layer of the liquid metal as a two-dimensional electron gas (obeying the Fermi-Dirac statistics) and define the surface tension as a negative pressure of this electron gas. Their work is severely criticized by Samoilovitch² who points out that the pressure of the electron gas must be positive and therefore Gogate and Kothari should have obtained *negative* values for the surface tension.

Dorfman³ deduces positive surface tension of metals from the electrostatic energy of the double layer on their surface; but again Samoilovitch shows that if, in addition to the electrostatic forces, the change of the kinetic energy of electrons is taken into consideration (according to the Thomas-Fermi theory), *negative* values are obtained for the surface tension of metals.*

Samoilovitch² succeeds in obtaining positive values for the surface tension of metals only because he introduces Weizsaecker's correction;⁴ Brager and Schuchovitzky⁵ point out that the introduction of this correction cannot be regarded as justified and that without it *negative* values of surface tension of metal would be obtained.

Brager and Schuchovitzky⁵ propose two approaches which would lead to positive values for the surface tension of metals.

The first approach is wave mechanical; from this point of view the authors consider the consequences of dividing a piece of metal into two parts (thus increasing its surface). They assume that there are two effects which result from such a division. The first effect is due to the wave properties of the electron; "as its energy spectrum must be discrete in a restricted volume of any size, a decrease in volume is

followed by a rise of all energy levels and therefore the energy of all electrons in the metal is increased. On the other hand, the division of a piece of metal into two parts brings about a doubling of the number of levels." According to the authors' calculations "the first effect is larger, so that the kinetic energy of the electrons increases on dispersion of the metal." They consider it to be the main physical reason for the high surface tension of metals.

The calculated values presented by Brager and Schuchovitzky are, however, in complete disagreement with the experimental data (most of them are about $2\frac{1}{2}$ times too high); the authors try to save the theory by assuming that the effective mass of electrons in metals is about $2\frac{1}{2}$ larger—which is obviously an unjustified generalization. The present author's opinion is that the theoretical figures obtained by Brager and Schuchovitzky may be due to the overestimation of their first effect in comparison with the second.

The second approach proposed by Brager and Schuchovitzky is the molecular orbitals method. No figures are given by the authors, and they themselves admit (see footnote in their paper) that this approach in principle gives negative surface tensions for all non-metals. There is no doubt, therefore, that this approach cannot lead to the main cause of the surface tension in general.

The present author wishes to make the following general comment.

The main cause of the surface tension of all liquids (and solids), whether metallic or not, is the same, *viz.*, *the total surface energy is determined by the amount of energy required to bring the molecules or atoms (and electrons) from the bulk of the condensed phase to its free surface, while enlarging the surface area.* In monatomic non-metallic liquids, and in organic liquids having no dipoles, this energy can be calculated directly from the heat of vaporization at absolute zero and from the configuration of nearest neighbors. In the case of metals the change of the kinetic energy of electrons must be considered in addition. Now, the latter is proportional to the density ρ of the electrons (to $\rho^{\frac{1}{3}}$ according to the Thomas-Fermi theory). Because the surface of

¹ D. V. Gogate and D. S. Kothari, *Phil. Mag.* **20**, 1136 (1935).

² A. Samoilovitch, *Acta Physicochimica U.S.S.R.* **20**, 97 (1945).

³ T. G. Dorfman, *Comptes Rendus* **41**, 386 (1943); compare, also, (5).

* Compare also reference 5, p. 13.

⁴ C. F. Weizsaecker, *Zeits. f. Physik* **96**, 431 (1935).

⁵ A. Brager and A. Schuchovitzky, *Acta Physicochimica U.S.S.R.* **21**, 13 (1946).

the physical discontinuity (the surface of the liquid) is not infinitely sharp, but remains undefined within 1-2 atomic distances,⁶ the average density in the surface region must be lower than that in the bulk, even if we allow for the slight contraction of the interatomic distances which is likely to occur in the surface layer.⁷ Therefore, the change in the kinetic energy of free electrons connected with their transfer from the bulk into the surface must contribute a negative term to the total surface energy.

Let us present a rough example of one of the possible ways of calculating this term and thus of getting at the value of the surface tension of metals.

Let us assume that the ratio of the densities of electrons in the surface and in the bulk is roughly determined by the ratio of number of atoms in the configuration volume unit, i.e., by $(Z_a+1):(Z_i+1)$, then the ratio of respective electron densities would be

$$\frac{\rho_A}{\rho_i} = \frac{(Z_a+1)}{(Z_i+1)}, \quad (7)$$

and the difference of the kinetic energy of the

electrons in the surface layer and in the bulk

$$\Delta U_{el} = E_i - E_a = \frac{3}{8}E_f - \frac{3}{8}E_f \left[\frac{(Z_a+1)}{(Z_i+1)} \right]^{\frac{3}{2}}, \quad (8)$$

where E_f is the Fermi energy.

Substituting numerical values we obtain

for Na, with $Z_i=8$, $Z_a=6$, $E_f=3.12$ ev,

$$U_{el} = 2340 \text{ cal./molar surf.}$$

for Ag, with $Z_i=12$, $Z_a=9$, $E_f=5.51$ ev,

$$U_{el} = 4770 \text{ cal./molar surf.}$$

which, subtracted from the respective $(Z_i - Z_a/Z_i)L_0$ values, give the following total surface energies:

for Na:

$$\begin{aligned} \sigma_M - T(d\sigma_M/dT) &= (8-6)/8 \times 26120 - 2340 \\ &= 4190 \text{ cal./mole surf.} \end{aligned}$$

for Ag:

$$\begin{aligned} \sigma_M - T(d\sigma_M/dT) &= (12-9)/12 \times 68740 - 4770 \\ &= 12415 \text{ cal./mole surf.} \end{aligned}$$

The measured values are 4400 cal./mole surf. and 11300 cal./mole surf., respectively.

The present author has no doubt that better ways of calculation of the electron effect on the surface tension of metals can be formulated. He thinks, however, that efforts should be abandoned to consider the presence of free electrons in metals as the main physical cause of their "high" surface tension.

⁶ Compare, e.g., N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1939), p. 6.

⁷ J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. London (A) 121, 247 (1928).