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Abstract

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TEMPERATURE DEPENDENCE OF THE SURFACE TENSION OF METALS

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The surface tension of many liquid metals is at present known fairly reliably; however, the temperature coefficients of surface tension, $d\sigma/dT$, found experimentally by various authors show a large scatter. Sufficiently well-founded calculations of $d\sigma/dT$ for metals are lacking in the literature.

In ([1]) one of us calculated $d\sigma/dT$ for a number of metals without taking into account the anharmonicity of ion vibrations and the thermal smearing of the Fermi energy. As approximate calculations ([2]) have shown, the effect of anharmonicity makes a noticeable contribution to $d\sigma/dT$.

In the present article, on the basis of the statistical electron theory of the surface tension of metals developed in ([1]), $d\sigma/dT$ for metals is calculated with allowance for the anharmonicity of ion vibrations and the Fermi–Dirac distribution function for the electron gas at $T \neq 0$. According to ([2]), the free energy of the vibrational motion of metal ions at $T \gg \theta$, with allowance for anharmonicity, is determined by the formula

$$F(\infty) = -3kT \ln \frac{kT}{\hbar\omega(\infty)} - 3kT^2 g(\infty), \tag{1}$$

where $g(\infty) = 5k\beta^2/6m\omega^6(\infty)$; $\beta = -\frac{1}{2}(d^3E/dr^3)_{r=a}$ is the first anharmonicity coefficient, related to the thermal coefficient of linear expansion α_l by the relation $\alpha_l = k\beta/am^2\omega^4(\infty)$; $a = 2\overline{R}$ is the mean distance between ions ($\overline{R}$ is the equilibrium radius of the elementary sphere ([1]); θ is the Debye temperature).

In the k-plane of the transition layer, respectively, we have:

$$F(\varepsilon) = -3kT \ln \frac{kT}{\hbar\omega(\varepsilon)} - 3kT^2 g(\varepsilon). \tag{2}$$

The temperature contribution to σ, on the basis of the isotropic model of a metal, is determined by expression ([1])

$$\sigma^{(T)} = \int_{-\infty}^{x_\Gamma} [F(x) - F(\infty)] n_v(x)\, dx, \tag{3}$$

where $n_v(x)$ is the number of ions in 1 cm^3 of metal; x_Γ is the coordinate of the Gibbs dividing surface.

Substituting (1) and (2) into (3) and expressing $\omega(\varepsilon)/\omega(\infty)$ and $g(\varepsilon)/g(\infty)$ through the function $\chi_i(\varepsilon)$, which determines the course of the potential and electron density of the metal in the transition layer, we obtain

$$\sigma^{(T)} = -0.9kTSN\frac{D}{A}\int_{-\infty}^{\varepsilon_\Gamma}\left(1-\frac{\varepsilon}{b}\right)^{-6} d\varepsilon -$$

$$-3.6SD\left(\frac{k}{\hbar}\alpha_l \overline{R}\theta T\right)^2 \int_{-\infty}^{\varepsilon_\Gamma}\left(1-\frac{\varepsilon}{b}\right)^{-6} d\varepsilon, \tag{4}$$

where $S = (3\pi/2'^2)^{1/2}(e/a_0V_i)^{1/4}a_0$; $b = 2(125/3)^{1/3}$; $\varepsilon_r = x_r/S = -0.106$; the remaining notation is the same as in (1).

Having carried out a simple integration and taking into account the change in the number of particles per 1 cm^2 of surface as a result of the expansion of the metal, in the formula for σ we obtain the following expression for the temperature dependence $d\sigma/dT$ of metals due to the ionic component of the metal:

$$\left(\frac{d\sigma}{dT}\right)_{\text{ion}} = -\left\{2\alpha_l\sigma + 0.81SD\left[\frac{R}{A} + 8T\left(\frac{k}{\hbar}\alpha_l\bar{R}\theta\right)^2\right]\right\}, \tag{5}$$

where R is the universal gas constant, and D is the density of the liquid metal.

We shall now calculate the contribution to $d\sigma/dT$ from the electronic subsystem of the metal. As is known ([3]), at a temperature much lower than the degeneracy temperature of the electron gas, the free energy per particle is

$$F \simeq \frac{3}{5}\mu_0 - \frac{\pi^2}{4}\frac{k^2T^2}{\mu_0}, \tag{6}$$

where $\mu_0 = eV_i = \frac{5}{3}k\rho^{2/3}(\infty)$ is the Fermi energy.

Consequently, the temperature smearing of the Fermi boundary gives an additional free energy of the electron

$$\Delta F = -\frac{\pi^2}{4}\frac{k^2T^2}{\mu_0}. \tag{7}$$

The volume density of this additional energy in any plane of the metal–vacuum transition layer will be

$$w_p = -\frac{\pi^2}{4}\frac{k^2T^2}{\mu_0(x)}\rho(x) = -\frac{\pi^2}{4}\frac{k^2T^2}{\mu_0}\rho^{2/3}(\infty)\rho^{1/3}(x), \tag{8}$$

where $\rho(x)$ is the volume density of the electron gas. Therefore the excess free energy associated with the smearing of the Fermi boundary in the inner region of the metal will give the following contribution to σ of the metal:

$$\Delta\sigma_i^{(p)} = -\frac{\pi^2k^2T^2}{4\mu_0}\rho^{2/3}(\infty)\int_{-\infty}^{x_r}\left[\rho_i^{1/3}(x) - \rho_i^{1/3}(\infty)\right]\,dx. \tag{9}$$

The outer part of the electron-density distribution ($x \geq x_r$) will give a contribution to σ

$$\Delta\sigma_e^{(p)} = -\frac{\pi^2k^2T^2}{4\mu_0}\rho^{2/3}(\infty)\left\{\int_{x_r}^{0}\left[\rho_i^{1/3}(x) - \rho_e^{1/3}(\infty)\right]\,dx + \int_0^{\infty}\left[\rho_e^{1/3}(x) - \rho_e^{1/3}(\infty)\right]\,dx\right\}. \tag{10}$$

Summing (9) and (10) and passing to the dimensionless variable $\varepsilon = x/S$ and the functions $\chi_i(\varepsilon)$ and $\chi_e(\varepsilon)$, we obtain the total contribution to σ of the metal caused by the temperature dependence of the Fermi energy

$$\Delta\sigma_p = -\frac{\pi^2k^2T^2}{4\mu_0}S\rho(\infty)\left\{\int_{-\infty}^{\varepsilon_r}\left[\chi_i^{1/2}(\varepsilon) - 1\right]\,d\varepsilon + \int_{\varepsilon_r}^{0}\left[\chi_i^{1/2}(\varepsilon) - \frac{\rho_e(\infty)}{\rho_i(\infty)}\right]\,d\varepsilon + \int_0^{\infty}\left[\chi_e^{1/2}(\varepsilon) - \frac{\rho_e(\varepsilon)}{\rho_i(\infty)}\right]\,d\varepsilon\right\}, \tag{11}$$

or, in view of the fact that $\rho_i(\infty) = Z/\Omega$ and $\rho_e(\infty) = 0$, we have:

$$\Delta\sigma_p = -\frac{\pi^2k^2T^2}{4\mu_0}S\frac{Z}{\Omega}\left\{\int_{-\infty}^{\varepsilon_r}\left[\chi_i^{1/2}(\varepsilon) - 1\right]\,d\varepsilon + \int_{\varepsilon_r}^{0}\chi_i^{1/2}(\varepsilon)\,d\varepsilon + \int_0^{\infty}\chi_e^{1/2}(\varepsilon)\,d\varepsilon\right\}. \tag{12}$$

Here Z is the average number of free electrons per metal atom; $\Omega = A/DN$ is the volume of the elementary sphere,

$$\chi_i(\varepsilon) = 1 - \frac{1 - \chi(0)}{(1 - \varepsilon/b)^6} \quad \text{for } \varepsilon \leqslant 0; \tag{13}$$

$$\chi_e(\varepsilon) = \frac{\chi(0)}{(1 + \varepsilon/b)^4} \quad \text{for } \varepsilon \geqslant 0, \tag{14}$$

where $\chi(0) = 3/5$.

Expanding $\chi_i^{1/2}(\varepsilon)$ in a series and integrating (12), we find

$$\Delta\sigma_p = -9.96 S \frac{Z}{\Omega} \frac{k^2 T^2}{\mu_0}. \tag{15}$$

Table 1

Results of calculations of $d\sigma/dT$ by formula (20)

Metal	Z	σ	T_S	V_a	T	$d\sigma/dT$, erg/cm^2· deg, calc.	$d\sigma/dT$, erg/cm^2· deg, exp.
Li	1	398	453	13.00	453	−0.117	−0.14
Na	1	196	370	23.71	370	−0.072	−0.05–(−0.10)
K	1	101	335.3	47.33	335.3	−0.042	−0.06–(0.11)
Rb	1	77	311.5	57.95	311.5	−0.035	–
Cs	1	60	301.5	72.39	301.5	−0.030	−0.046
Cu	1	1350	1356	7.21	1356	−0.186	−0.17–(−0.31)
Ag	1	923	1233	10.28	1233	−0.142	−0.13
Au	1	1128	1336	11.42	1393	−0.142	−0.10
Be	2	1100	1623	6.34	1773	−0.184	–
Mg	2	540	924	15.59	924	−0.098	−0.34
Ca	2	420	1123	26.02	1123	−0.071	–
Sr	2	272	1020	33.45	1020	−0.058	–
Ba	2	248	1123	38.37	1123	−0.054	–
Zn	2	740	693	9.17	693	−0.146	−0.09–(−0.25)
Cd	2	606	593.9	14.04	612	−0.117	Positive
Hg	2	465	234.3	14.81	293	−0.156	−0.17–(−0.22)
Al	3	840	933	10.00	933	−0.134	−0.14
Ga	3	706.6	302.8	11.44	302.8	−0.175	−0.000647
In	3	570	429	15.74	429	−0.117	−0.085 – (−0.10)
Tl	3	464.5	576.5	18.53	576.5	−0.076	−0.080
Sn	2	549	504.8	16.93	504.8	−0.108	−0.072 – (−0.18)

Metal	Z	σ	T_S	V_a	T	$d\sigma/dT$, erg/cm^2· deg, calc.	$d\sigma/dT$, erg/cm^2· deg, exp.
Pb	2	450	600.4	19.35	600.4	−0.089	−0.077 – (−0.12)
Sb	3	348	903	18.76	913	−0.079	−0.06
Bi	3	376	544	20.76	544	−0.081	−0.042 – (−0.075)
Cr	2	1590	1888	8.67	1900	−0.166	–
Co	2	1640	1763	7.81	1763	−0.175	−0.92
Ni	2	1485	1725	7.56	1725	−0.174	−0.98
Rh	2	1940	2239	9.66	2239	−0.165	–
Pd	2	1470	1828	9.97	1828	−0.154	–

The term corresponding to the contribution (15) in the temperature coefficient of the surface tension of metals will be

$$\left(\frac{d\sigma}{dT}\right)_{\text{el}} = -19.92\,SZD\,\frac{R}{A}\,\frac{kT}{\mu_0}. \tag{16}$$

Taking into account the contribution to $d\sigma/dT$ from the ionic subsystem (5), finally the temperature coefficient of the surface tension of metals can be represented in the form

$$\left(\frac{d\sigma}{dT}\right) = \left(\frac{d\sigma}{dT}\right)_{\text{ion}} + \left(\frac{d\sigma}{dT}\right)_{\text{el}}$$

or

$$\frac{d\sigma}{dT} = -\left\{2\alpha_l\sigma + 0.81SD\left[\frac{R}{A} + 8T\left(\frac{k}{\hbar}\alpha_l R\bar{\theta}\right)^2 + 24.6Z\,\frac{R}{A}\,\frac{kT}{\mu_0}\right]\right\}. \tag{17}$$

The first three terms in (17) are, in order of magnitude, approximately the same; the last is almost one order lower.

The first and third terms in (17) are due to the anharmonicity of ion vibrations and the associated expansion of the metal and change in the ion energy; the second is due to the change in the character of the ion vibrations in the transition layer in connection with the presence of a density gradient of the electron liquid;

and, finally, the last is due to the smearing of the Fermi energy. The main contribution to $d\sigma/dT$ is due to the anharmonicity of ion vibrations.

In order to put formula (17) into a form convenient for practical calculations, we shall use the well-known approximations of Grüneisen and Lindemann [4]

$$\int_0^{T_s} \alpha_l dT = \bar{\alpha}_l T_s \simeq 0.022, \tag{18}$$

$$\theta = 137 \left(T_s / A V_a^{2/3}\right)^{1/2}, \tag{19}$$

where T_s is the melting temperature, V_a is the atomic volume, and, taking into account that $\mu_0 = 26.07\,(Z/V_a)^{2/3}$ eV, we finally obtain

$$\frac{d\sigma}{dT} = -\left\{\frac{0.044\sigma}{T_s} + \frac{0.328}{V_a}\left(\frac{V_a}{Z}\right)^{1/6}\left[1 + 0.832\,\frac{T}{T_s} + 0.82\cdot 10^{-4}\left(\frac{Z}{V_a}\right)^{1/3} V_a T\right]\right\}. \tag{20}$$

The values of $d\sigma/dT$ calculated by formula (20) agree satisfactorily with the experimental data for non-transition metals (see Table 1).

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CITED LITERATURE

[1] S. N. Zadumkin, *Fiz. met. i metalloved.*, **11**, No. 3, 331 (1961).
[2] S. N. Zadumkin, *ZhFKh*, **33**, No. 11, 2601 (1959).
[3] J. Mayer, M. Goeppert-Mayer, *Statistical Mechanics*, IL, 1952, p. 386.
[4] *Handbook: Metallurgy and Heat Treatment*, **1**, 1960.

Note: Figure translations are in progress. See original paper for figures.