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The work function of an electron gas

D. E. G. WILLIAMS

Department of Physics, Loughborough University, Loughborough, LE11 3TU,
England

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Abstract. An investigation of the temperature variation of the work function of an electron gas is made by collective electron theory methods.

In the conventional approach to the collective electron theory (e.g. Stoner 1938) the Helmholtz free energy of the electron gas F is written down in terms of the Gibbs free energy G and the thermodynamic potential $\Omega (= -PV$, where P and V are pressure and volume respectively) as

$$F = G + \Omega.$$

Ω is deduced from statistical mechanics as

$$-kT \int_0^{\infty} Vn(E) \ln [1 + \exp\{(\mu - E)/kT\}] dE$$

where $n(E)$ is the density of states in energy per unit volume for the electron gas and μ is the chemical potential of the electron gas. G is taken as $N\mu$ where N is the number of electrons in the gas, and μ is measured relative to the energy of the bottom of the band. In the free electron theory of metals this is a quite satisfactory zero of energy since the electrons move in a zero potential and the energy of the bottom of the band is unaltered by, for example, changes in volume of the metal. When the same concept of an energy zero at the bottom of the band is applied to a more realistic model of a solid, where the electron is moving in a potential which is periodic with the periodicity of the crystal lattice, it would seem likely that the choice of energy zero at the bottom of the energy band is less appropriate than in the case of the free electron gas. The volume of the solid and hence the periodicity of the lattice can be altered, for example, by altering its temperature, and there is no good reason to believe that the energy of the bottom of the band remains constant when the temperature of the solid is raised. Provided that no allotropic phase transformations occur, the symmetry of the crystal is not usually altered by raising its temperature and thus increasing its volume, so that we would not expect the shape of the band to alter appreciably as the temperature is raised.

In order to describe the electron gas, the most appropriate model would thus seem to be one in which the density of states curve has a fixed shape, but whose bottom can 'drift' in energy as the volume of the crystalline lattice is altered. In order to make the meaning of the Gibbs free energy more precise, we have to define a fixed zero of energy, and measure the Gibbs free energy from that zero rather than from the bottom of the band. It is obviously convenient to choose the zero of energy as that of an electron at rest at the surface of the solid; in this case if the energy of the bottom of the density of states curve relative to this zero is $-W$, then the Gibbs free energy of the electron gas may be written as

$$\begin{aligned} G &= N(\mu - W) \\ &= -N\phi \end{aligned}$$

where ϕ is the work function of the electron gas. The variation with temperature of the work function may be written as

$$\frac{d\phi}{dT} = \left(\frac{\partial\phi}{\partial T}\right)_V + \left(\frac{\partial\phi}{\partial V}\right)_T \frac{dV}{dT}$$

and since, if the solid has constant volume, W is constant, the first term is merely

$$\left(\frac{\partial\phi}{\partial T}\right)_V = - \left(\frac{\partial\mu}{\partial T}\right)_V$$

so that

$$\frac{d\phi}{dT} = - \left(\frac{\partial\mu}{\partial T}\right)_V + \left(\frac{\partial\phi}{\partial V}\right)_T \frac{dV}{dT}$$

We may write

$$\begin{aligned} \left(\frac{\partial\phi}{\partial V}\right)_T &= - \frac{1}{N} \left(\frac{\partial G}{\partial V}\right)_T = - \frac{1}{N} \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T \\ &= \frac{1}{\chi N} \end{aligned}$$

where χ is the isothermal compressibility. Hence we may write

$$\begin{aligned} \frac{d\phi}{dT} &= - \left(\frac{\partial\mu}{\partial T}\right)_V + \frac{1}{\chi N} \frac{dV}{dT} \\ &= - \left(\frac{\partial\mu}{\partial T}\right)_V + \frac{\alpha V_0}{\chi N} \end{aligned} \quad (1)$$

where α is the coefficient of volume expansion and V_0 is the volume of the solid at 0 K. The first term in equation (1) has been evaluated for a free electron gas by Stoner (1936), subject to the condition that $(kT/\mu_0) \ll 1$, as

$$- \left(\frac{\partial\mu}{\partial T}\right)_V = \frac{\pi^2 k^2 T}{6 \mu_0}$$

which can be estimated as of the order of 10^{-6} eV K $^{-1}$ at room temperature (Williams and Goto 1970).

In order to obtain an order of magnitude estimate of the second term in equation (1), let us assume that, for tungsten there are six electrons per atom in the electron gas, so that

$$\frac{N}{V_0} = \frac{6 \times 6.023 \times 10^{23}}{9.63} \text{ ml}^{-1}$$

and take the room-temperature values, $\chi \sim 3 \times 10^{-13}$ dyn cm $^{-2}$ and $\alpha \sim 1.3 \times 10^{-5}$ K $^{-1}$. In this case

$$\frac{\alpha V_0}{\chi N} \sim 8 \times 10^{-5} \text{ eV K}^{-1}.$$

This term will obviously dominate equation (1) except at high temperatures, so that, for tungsten

$$\frac{d\phi}{dT} \sim \frac{\alpha V_0}{\chi N} \sim 8 \times 10^{-5} \text{ eV K}^{-1}.$$

The numerical value obtained compares quite favourably with the experimental values, $d\phi/dT \sim 6 \times 10^{-5} \text{ eV K}^{-1}$, for tungsten, given by Fomenko (1966) and by Kruger and Stabenow (1935). A similar calculation for tantalum, assuming 5 electrons per atom, gives $d\phi/dT \sim 9 \times 10^{-5} \text{ eV K}^{-1}$ compared with Kruger and Stabenow's result $d\phi/dT \sim 6 \times 10^{-5} \text{ eV K}^{-1}$. For molybdenum the comparison is not so good since Kruger and Stabenow did not obtain a significant result, while the value predicted from this model is $7 \times 10^{-5} \text{ eV K}^{-1}$.

Previous interpretations of the temperature variation of the work function (e.g. Seitz 1940) seem to have been directed towards obtaining a relation between experimental and theoretical values of the constant in the equation of thermionic emission, rather than towards obtaining an explicit expression for $d\phi/dT$.

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