The chemical potential of an electron gas

J. Phys. A: Gen. Phys., 1970, Vol. 3. Printed in Great Britain

The chemical potential of an electron gas

D. E. G. WILLIAMS and K. GOTO†

Department of Physics, Loughborough University, Leicestershire, England
MS. received 26th March 1970, *in revised form* 14th May 1970

Abstract. The effect of a change in volume on the chemical potential of an electron gas is investigated. It is found that an increase in volume generally gives rise to a decrease in chemical potential, the temperature coefficient of the chemical potential being of the same order of magnitude as the coefficient of volume expansion.

1. Introduction

The usual approach to the collective electron theory of metals (e.g. Stoner 1938) is through the grand partition function, and this results in the thermodynamic potential

$$\Omega = \Omega(T, V, \mu) = -PV(T, V, \mu)$$

where T is the temperature, V the volume, μ the chemical potential, and PV the product of pressure and volume of the electron gas. The expression for the Helmholtz free energy is then

$$F = G + \Omega = N\mu + \Omega$$

where G is the Gibbs free energy of the electron gas and N the number of electrons in it, and various measurable quantities are derived from this Helmholtz free energy, e.g. following Stoner, the magnetic susceptibility for paramagnetic materials is given by

$$\chi = -\left(\frac{\partial^2 F}{\partial H^2}\right)_{T,V} = -\left(\frac{\partial^2 \Omega}{\partial H^2}\right)_{T,V\mu}$$

where H is the magnetic field strength. The derived quantity is then used to predict, for example, the temperature variation of the measurable quantity.

The results of this technique do not take into account the variations in volume to which the electron gas is subject as its temperature alters—in terms of a very simple model, the electron gas is contained within a container (the crystal) which expands as the temperature is increased. It has only recently been pointed out (Fischer *et al.* 1969) that this expansion should be taken into account by considering the complete derivative of the measurable quantity. Thus, if our measurable quantity is denoted by A, the measured temperature variation of A should be written as

$$\frac{dA}{dT} = \left(\frac{\partial A}{\partial T}\right)_V + \left(\frac{\partial A}{\partial V}\right)_T \frac{dV}{dT}. \tag{1}$$

If the number of electrons in the electron gas altered appreciably with a change in temperature, this equation would need to be rewritten as

$$\frac{dA}{dT} = \left(\frac{\partial A}{\partial T}\right)_{N,V} + \left(\frac{\partial A}{\partial V}\right)_{T,N} \frac{dV}{dT} + \left(\frac{\partial A}{\partial N}\right)_{V,T} \frac{dN}{dT}$$

† Now at the Research Institute for Scientific Measurements, Tohoku University, Sanjyo-machi, Sendai, Japan.

but we concern ourselves here only with electron gases containing a fixed number of electrons.

2. The free-electron gas

In the case of the free-electron gas we have the density of states per unit energy range, per unit volume:

$$n(E) = aE^{1/2}$$

where a is a constant, independent of volume. Hence if a volume V contains N free electrons, at zero temperature we have

$$\frac{N}{V} = \int_0^{\mu_0} aE^{1/2}\,\mathrm{d}E$$

where μ_0 is the chemical potential of the electron gas at $T = 0$. On integrating this expression we find

$$\mu_0 = \left(\frac{3}{2a}\frac{N}{V}\right)^{2/3}$$

so that, at $T = 0$,

$$\left(\frac{\partial\mu}{\partial V}\right)_{T=0} = -\frac{2}{3}\frac{\mu_0}{V}.$$

For $T > 0$, we have

$$\frac{N}{V} = \int_0^\infty \frac{aE^{1/2}\,\mathrm{d}E}{\exp\{(E-\mu)/kT\}+1}$$

which, in the notation used by Landsberg (1961), may be written as

$$\frac{N}{V} = a(kT)^{3/2}\,\Gamma\left(\frac{3}{2}\right)I(\eta, \tfrac{1}{2}, +) \tag{2}$$

where $\Gamma(3/2)$ is a gamma function, $\eta = \mu/kT$, and

$$I(c, s, \pm) = \frac{1}{\Gamma(s+1)}\int_0^\infty \frac{x^s\,\mathrm{d}x}{\exp(x-c)\pm 1}$$

where $s > -1$. On differentiating equation (2) with respect to η, we find

$$-\frac{N}{V^2}\left(\frac{\partial V}{\partial \eta}\right)_{T,N} = a(kT)^{3/2}\,\Gamma(1/2)I(\eta, -\tfrac{1}{2}, +)$$

which may be rewritten as

$$\left(\frac{\partial\mu}{\partial V}\right)_{T,N} = -\frac{akT}{V}\frac{\Gamma(3/2)}{\Gamma(1/2)}\frac{I(\eta, \tfrac{1}{2}, +)}{I(\eta, -\tfrac{1}{2}, +)}.$$

For $\eta \gg 1$, the right-hand side may be expanded (Landsberg 1961—§ 31) to give

$$\left(\frac{\partial\mu}{\partial V}\right)_{T,N} = -\frac{2\mu_0}{3V}\left\{1+\frac{\pi^2}{6}\left(\frac{kT}{\mu_0}\right)^2 + \ldots\right\}$$

so that, for $\mu \gg kT$, we may say that $(\partial\mu/\partial V)_{T,N}$ is effectively independent of temperature. We would therefore expect that we could assume with confidence that $(\partial\mu/\partial V)_{T,N}$ is independent of temperature to temperatures at least as high as room temperature, and possibly to much higher temperatures.

On substituting in an equation for the chemical potential analogous to equation (1), we find that

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = \left(\frac{\partial\mu}{\partial T}\right) - \frac{2}{3}\frac{\mu_0}{V}\frac{\mathrm{d}V}{\mathrm{d}T} \tag{3}$$

but the coefficient of volume expansion $\alpha = (1/V)(\mathrm{d}V/\mathrm{d}T)$, with the result that

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = \left(\frac{\partial\mu}{\partial T}\right)_V - \frac{2}{3}\alpha\mu_0. \tag{4}$$

The first term of the right-hand side of this equation is given for the free-electron gas as

$$\left(\frac{\partial\mu}{\partial T}\right)_V = -\frac{\pi^2}{6}\frac{k^2 T}{\mu_0} + O(T^3).$$

The relative importance of the two terms in equation (3) can be roughly estimated by the observations that estimates of μ_0 for metals give values of about 5 eV, that Boltzmann's constant $k \sim 10^{-4}$ eV K^{-1} and that, for metals, the coefficient of volume expansion at $T = 300$ K is about 3×10^{-5} K^{-1}. Using these figures gives

$$\left(\frac{\partial\mu}{\partial T}\right)_V \sim -10^{-6}\text{ eV K}^{-1}; \qquad \frac{2}{3}\alpha\mu_0 \sim 10^{-4}\text{ eV K}^{-1} \tag{5}$$

so that, even when $T = 300$ K, the first term only represents about 1% of the temperature variation of μ.

We can thus say that, for a free-electron gas whose volume is expanded arbitrarily as the temperature increases, the temperature variation of the chemical potential is dominated by the expansion of its enclosure, even when the coefficient of this is of the order of 10^{-5} K^{-1}. This can be explained physically by recollecting that the separation of the energy states in the free-electron gas is proportional to $V^{-2/3}$; the electron concentration is proportional to V^{-1}. Hence, when the volume of the enclosure alters, these two quantities do not alter so as to cancel out each others' effects, and consequently the chemical potential alters significantly with increase in temperature.

3. The general case

The generalization of the collective electron theory is obtained by introducing the general density of states $n(E)$ per unit energy range per unit volume. In this case we may write, for $T = 0$,

$$\frac{N}{V} = \int_0^{\mu_0} n(E)\,\mathrm{d}E$$

so that

$$-\frac{N}{V^2}\,\mathrm{d}V = n(\mu_0)\,\mathrm{d}\mu_0$$

i.e.

$$\left(\frac{\partial\mu_0}{\partial V}\right)_{T=0} = -\frac{N}{V^2 n(\mu_0)}.$$

Hence, assuming that this quantity is appreciably unaltered by increasing temperature,

and that the density of states is independent of volume, we have

$$\left(\frac{\partial \mu}{\partial V}\right)_T \frac{\mathrm{d}V}{\mathrm{d}T} = \frac{-Q_0 \alpha}{n(\mu_0)}$$

where Q_0 is the electron concentration for $T = 0$. It is not a simple matter to generalize from this equation; in the case $n(E) = aE^r$ then $Q_0/n(\mu_0) = \mu_0/(r+1)$ will be of the same order of magnitude as μ_0, and less than μ_0 (unless $r < 0$). If we accept this as a general form we may write

$$\left(\frac{\partial \mu}{\partial V}\right)_T \frac{\mathrm{d}V}{\mathrm{d}T} = -c\alpha\mu_0$$

where $c < 1$ is a constant for a given Q_0 and $n(E)$. The first term in the equation for $\mathrm{d}\mu/\mathrm{d}T$ is given by Stoner (1936) as

$$\left(\frac{\partial \mu}{\partial T}\right)_V = -\frac{\pi^2}{3} k^2 T \left(\frac{1}{n}\frac{\partial n}{\partial E}\right)_{\mu_0}$$

so that

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = -\frac{\pi^2 k^2 T}{3} \left(\frac{1}{n}\frac{\partial n}{\partial E}\right)_{\mu_0} - c\alpha\mu_0. \qquad (6)$$

Once more it seems reasonable that the second term should be larger, so that we can say that, in general, μ decreases as the temperature increases. The rate of decrease is of the same order of magnitude of the coefficient of volume expansion which, for metals, is 10^{-5} K^{-1}.

4. Application

The direct method of finding the chemical potential of electron gases in metals is by measurement of the contact potential. The information obtained from such measurements is often contradictory (e.g. Fomenko 1966) and figures for the variation of contact potential with temperature are not readily available. On the other hand the work function ϕ of a metal is defined by

$$\phi = |W - \mu|$$

where W is the energy of the bottom of the energy band: if we assume W is independent of T, then

$$\frac{\mathrm{d}\phi}{\mathrm{d}T} = -\frac{\mathrm{d}\mu}{\mathrm{d}T}$$

so that the work function should vary with temperature in the opposite sense to the variation of chemical potential with temperature. Some measurements of the variation of the work function with temperature are available (Fomenko 1966, Kruger and Stabenow 1935), and for polycrystalline tungsten the value is about 6×10^{-5} eV K^{-1}. (Measurements on single crystal specimens show that $\mathrm{d}\phi/\mathrm{d}T$ depends on the face of the crystal from which the emission takes place, but the interpretation of single crystal measurements demands a more sophisticated model than the collective electron gas.) The order of magnitude agreement of measured values of $\mathrm{d}\phi/\mathrm{d}T$ with the predicted value of $\mathrm{d}\mu/\mathrm{d}T$ (equation (5)) is interesting: one possible contribution to the variation of ϕ with T is the thermoelectric potential between the two electrodes in a

measuring circuit. The contribution from this to ϕ would be

$$\int_{T_1}^{T_2} \left(\int_0^{T'} \frac{\sigma_T \, \mathrm{d}T}{T} \right) \mathrm{d}T'$$

where σ_T is the thermoelectric Thomson coefficient. It is difficult to estimate the importance of this contribution in thermionic experiments, but if measurements were made of the contact potential over a small range of temperature about room temperature, estimates of its magnitude could be made. Typically, at $0\,°C$, this contribution is about 10^{-6} eV K^{-1}, i.e. a factor of ten smaller than the variation of μ due to the volume change.

References

FISCHER, O., PETER, M., and STEINEMANN, S., 1969, *Helv. phys. Acta,* **42,** 459.
FOMENKO, V. S., 1966, *Handbook of Thermionic Properties* (New York: Plenum).
KRUGER, F., and STABENOW, G., 1935, *Ann. Phys.,* **22,** 713.
LANDSBERG, P. T., 1961, *Thermodynamics* (New York: Interscience), §§ 28, 31.
STONER, E. C., 1936, *Proc. R. Soc.* A, **154,** 656.
—— 1938, *Proc. R. Soc.* A, **165,** 372.