A Quantitative Model for the Thermocouple Effect Using Statistical and Quantum Mechanics

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Abstract. This paper employs statistical and quantum mechanics to develop a model for the mechanism underlying the Seebeck effect. The conventional view of the equilibrium criterion for valence electrons in a material is that the Fermi Energy should be constant throughout the system. However, this criterion is an approximation and it is shown to be inadequate for thermocouple systems. An improved equilibrium criterion is developed by applying statistical and quantum mechanics to determine the total flow of electrons across an arbitrary boundary within a system. Dynamic equilibrium is then considered to be the situation where the Fermi Energy either side of the boundary is such that the flow of electrons in each direction is the same. This equilibrium criterion is then applied to the conditions along the thermocouple wires and at the junctions in order to generate a model for the Seebeck effect. The equations involved for calculating the electronic structure of a material cannot be solved analytically, so a solution is achieved using numeric models employing CASTEP code running on a Sun Beowulf cluster and iterative algorithms written in the Excel™ VBA language on a PC. The model is used to calculate the EMF versus temperature function for the gold versus platinum thermocouple, which is then compared with established experimental data.

1. INTRODUCTION

The behavior of electrons in a metal can be described using quantum mechanics, and in particular the many-body Schrödinger equation. From this, it is possible to develop a mathematical model that allows the Seebeck coefficient for thermocouples to be calculated from fundamental constants and empirical data on the variations of the density of the thermocouple wires with temperature. Although not covered in this paper, the variation of density with temperature may also be calculable using models derived from quantum mechanics leading to the prospect of being able to determine the relationship between a thermocouple's EMF and thermodynamic temperature from fundamental constants only. This will be described in a future paper.

The equations in the model cannot be solved analytically. However, developments in numerical quantum mechanics [1] and increases in computing power mean that it is now possible to generate accurate solutions numerically. The solutions are derived for the gold versus platinum thermocouple and

the predicted EMF-temperature characteristics are compared with published experimental data [2].

2. ELECTRONS IN A METAL

The outer electrons of a metal atom within the solid occupy energy states that are not associated with a particular atom. As a result, they are free to move throughout the metal under the influence of an applied field, thereby giving the characteristic high electrical conductivity associated with metals. This is the 'free-electron' model of electrons in a metal [3].

The movement of electrons within the metal is associated with a wave function that determines the probability of an electron being found at any point. The metal may be regarded as a potential well with sharp potential energy 'sides' at the surface of the metal caused by the short-ranging forces that act on the valence electrons to keep them within the metal. The wave function for the valence electrons satisfies Schrödinger's equation, leading to discrete and defined energy states for electrons within the metal whose

wave functions correspond to three-dimensional standing waves within the material. In addition to this further constrains are applicable to the many-electron system and in particular the Pauli exclusion principal, which states that only two electrons (with opposite spin) can occupy each energy state. In order to model the behavior of electrons in the metal we need to determine the DoS (density of states) and the distribution of electrons within these states (the probability that each state is occupied).

The density of states, DoS(E), for the valence electrons of energy E can be calculated by solving Schrödinger's equation for the discrete energy states. However, in the general many-body case, such a solution is impossible both analytically and numerically, mainly due to the complexity of the many-body wave function and the interactions that need to be considered (for example, each electron is effected by the potential field caused by each metal ion in the crystal and by each of the other valence electrons). Simplifications such as the equi-potential box model predict that the DoS varies with the square root of energy [4]. This simplified model is however quite inadequate and leads to results that are far from the measured values.

In order to solve the many-body Schrödinger equation we have used a method known as Density Functional Theory (the full methods are summarized in reference [1]) that includes all the interaction terms in the Schrödinger equation including the quantum mechanical interactions of exchange and correlation (exchange being the term that causes the Pauli exclusion principle). This will give us a reliable and accurate density of states for the metallic systems under consideration.

Given the DoS we then need to introduce the effects of temperature into the electronic system. The probability $p(E)$, that a state with energy E is occupied follows Fermi-Dirac statistics [4]:

$$p(E) = \frac{1}{e^{(E-E_0)/kT} + 1} \qquad (1)$$

where E_0 is the Fermi Energy, k is Boltzmann's constant, and T the absolute temperature. This function is a step function falling from unity (state occupied) to zero (states not occupied) at the Fermi Energy. The step 'edge' is sharp at 0 K (absolute zero) and becomes increasingly 'blurred' at higher temperatures.

2.1 Gold and Platinum

The overlap between the energy states for the 5d and 6s electrons in gold means that there are 11 valence electrons per metal ion (ten 5d and one 6s). The DoS function for the valence electrons in gold was calculated using CASTEP code [1] running on a Sun Beowulf cluster to produce a DoS data set at 0.065eV intervals. The underlying parabolic function for the 6s electrons predicted by the equi-potential box model can be discerned with the peak between 3 and 8 eV arising from the 5d electrons:
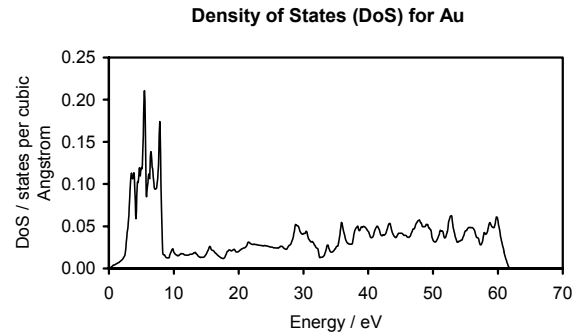

FIGURE 1: Density of States for Gold.

There are 10 valence electrons per metal ion in platinum (eight 5d and two 6s). The DoS function for platinum was calculated to produce a DoS data set at 0.072 eV intervals:
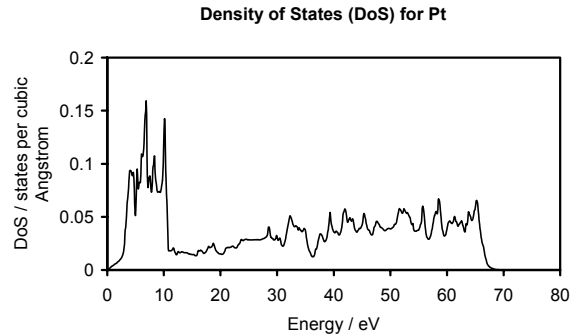

FIGURE 2: Density of States for Platinum.

2.2 Calculation of Fermi Level

The density of electrons of energy E can be determined by multiplying the density of states DoS(E) by the probability that the states are occupied $p(E)$. The density of the valence electrons is then the integral of this product and must equal the density of valence electrons determined from the atomic density.

For a neutral metal of density ρ, atomic mass A and with L valence electrons per metal ion we have:

$$\int_0^\infty DoS(E)\,p(E)\,dE = L\frac{\rho}{A}No \qquad (2)$$

where No is Avogadro's number. Temperature affects both the density ρ and the Fermi function $p(E)$. The Fermi Energy for a metal at a given temperature can be determined by evaluating both sides of Eq. (2) and iterating E_0 to find a value that makes these equal. This was accomplished using VBA Macros in Excel™ on a PC working with the DoS data sets. The results for gold and platinum are:
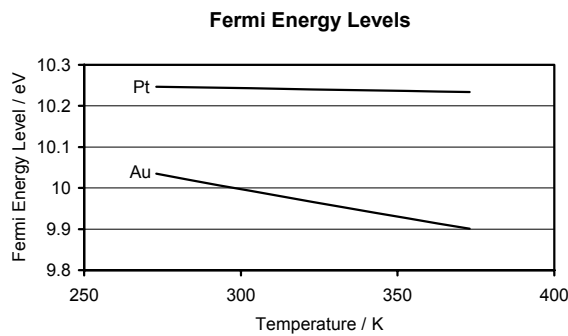
Fermi Energy Levels

FIGURE 3: Fermi Energies for Gold and Platinum

Eq. (2) applies only to neutral metals. Clearly, if additional electrons are added, the metal will become negatively charged, thereby reducing its potential. At the same time, the Fermi Energy will have to increase in order to accommodate the additional electrons. However, the change in Fermi Energy is vanishingly small for all reasonable metal potentials so that the Fermi Energy may reasonably be regarded as constant for a given metal at a specified temperature.

2.3 EMF and the Fermi Energy

It is worth reminding ourselves that the Fermi Energy has no physical significance except at absolute zero when it is the energy of the highest occupied state (although under certain circumstances it can be equated to the chemical potential of the system, but that is not necessary in the current work). Here, the Fermi energy is simply chosen as a convenient integration constant that produces an elegant form for the Fermi function, as shown in Eq. (1). It is then the energy at which the probability of the state being occupied is 0.5

EMF is defined as the tendency to push charge around a circuit. EMF is often considered to be the difference in Fermi Energy between two points in a circuit since it is this difference in Fermi Energy (and the corresponding difference in concentration of electrons at a given energy) that drives current around isothermal, homogeneous circuits. It must be remembered that EMF and Fermi Energy are not synonymous and the equality of the two only applies to isothermal, homogeneous circuits. However, since the terminals of any practical thermocouple measurement system will be at the same temperature and will be made of the same material, the EMF measured will be identical to the difference in Fermi Energies (subject to the isothermal and homogeneous proviso).

3. EQUILIBRIUM REQUIREMENTS

The accepted view of the behaviour of electrons in a circuit is that the equilibrium condition (no current flow) arises when the Fermi Energy is constant throughout the circuit. This is true at 0 K but is an approximation at all other temperatures. This can be seen to be true by considering an open thermocouple circuit exposed to a temperature gradient; if the Fermi Energy were constant throughout the circuit it would be the same at the open ends of the circuit and there would be no EMF, which we know is not the case. The fact that thermocouples generate EMFs demonstrates that the Fermi Energy is not, in general, constant within a circuit at equilibrium.

3.1 General Equilibrium Condition

Equilibrium within a circuit is actually a state of dynamic equilibrium. Valence electrons are in constant motion and the equilibrium condition in a circuit occurs when the current in one direction exactly balances the current in the opposite direction.

The potential and kinetic energies of the valence electrons can usefully be represented by an energy diagram. The thick line shows the potential energy of electrons, which changes abruptly at the metal surface. The gray shaded area shows the spread of quantised kinetic energies of the valence electrons within the metal. Some permitted energy states for electrons remain unoccupied or empty as shown in the conduction band:
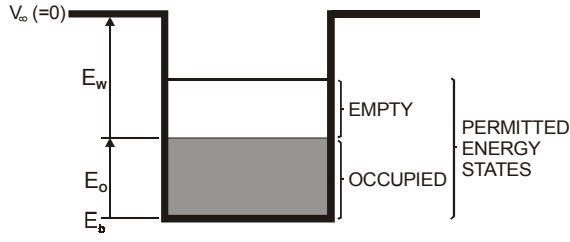
FIGURE 4: Electron Energy Diagram for a Neutral Metal

The general condition for equilibrium can be determined by considering the current flow across the interface between two metals at different temperatures (Figure 5). This equilibrium requirement can then be used to determine the EMF generated along the thermocouple wire exposed to a temperature gradient (same metal at different temperatures) and at a thermocouple junction (different metals at the same temperature).

FIGURE 5: Two Metals in Contact.

For valence electrons with energies between E and $E+dE$ in metal A, the rate of transfer of electrons (the current) across the interface to material B depends on:

1. The number of energy states in metal A = $DoS_A(E) \times V_A \times dE$

2. The probability that the states in metal A are occupied = $p(E, E_{0A}, T_A)$

3. The probability that the states in metal B are unoccupied = $1 - p(E, E_{0B}, T_B)$

4. The rate at which the electrons 'hit' the interface between A and B. This is proportional to the speed of the electrons and is inversely proportional to the volume of A. The probability of transfer is therefore proportional to these two terms i.e. $\propto \sqrt{E}/V_A$

The current flowing from A to B can be determined by integrating:

$$I_{AB} \propto \int_0^\infty DoS_A(E) V_A\, p(E, E_{0A}, T_A)\{1 - p(E + \delta V, E_{0B}, T_B)\}\frac{\sqrt{E}}{V_A}\, dE \quad (3)$$

A similar equation can be derived for the current flowing from B to A. The net current (difference between these) will lead to a change in δV that continues until the two currents are equal (dynamic equilibrium). The condition for equilibrium is therefore:

$$\int_0^\infty DoS_A(E)\, p(E, E_{0A}, T_A)\{1 - p(E + \delta V, E_{0B}, T_B)\}\sqrt{E}\,dE = $$
$$\int_0^\infty DoS_B(E)\, p(E, E_{0B}, T_B)\{1 - p(E - \delta V, E_{0A}, T_A)\}\sqrt{E}\, dE \quad (4)$$

The product of the $p(E)$ and $1-p(E)$ terms in Eq. (4) falls rapidly to zero away from the Fermi Energy, so only electrons near the Fermi Energy play any part in the current between the two metals.

4. CALCULATING EMFS

The equilibrium condition expressed in Eq. (4) can be used to calculate the contribution to the thermocouple EMF of the temperature gradient along the thermocouple wires and of the junctions. The thermocouple EMF is the sum of these two components.

4.1 EMF along the Wires

The general equilibrium condition developed above can be applied to the EMF generated along a homogeneous wire exposed to a temperature gradient:

FIGURE 6: Temperature Gradient along Metal

As $\delta T \rightarrow 0$ (and therefore δE_0 and $\delta V \rightarrow 0$) then:

$$p(E + \delta V, E_0 + \delta E_0, T + \delta T) = $$
$$P + \frac{\partial P}{\partial E}\delta V + \frac{\partial P}{\partial E_0}\delta E_0 + \frac{\partial P}{\partial T}\delta T, \quad (5)$$

where $P = p(E, E_0, T)$. The equilibrium requirement of Eq. (4) then becomes:

$$\int_0^\infty DoS(E) P\left\{1-\left(P+\frac{\partial P}{\partial E}\delta V+\frac{\partial P}{\partial E_0}\delta E_0+\frac{\partial P}{\partial T}\delta T\right)\right\}\sqrt{E} = \qquad (6)$$

$$\int_0^\infty DoS(E)\left\{P+\frac{\partial P}{\partial E}\delta V+\frac{\partial P}{\partial E_0}\delta E_0+\frac{\partial P}{\partial T}\delta T\right\}(1-P)\sqrt{E}\ dE$$

The symmetry of this equation means that many of the terms cancel out leaving:

$$\int_0^\infty DoS(E)\left\{\frac{\partial P}{\partial E}\delta V+\frac{\partial P}{\partial E_0}\delta E_0+\frac{\partial P}{\partial T}\delta T\right\}\sqrt{E}\ dE = 0 \qquad (7)$$

The δV and δE_0 terms can be eliminated:

$$\int_0^\infty DoS(E)\left\{\frac{\partial P}{\partial E}\frac{dV}{dT}\delta T+\frac{\partial P}{\partial Eo}\frac{dE_0}{dT}\delta T+\frac{\partial P}{\partial T}\delta T\right\}\sqrt{E}\ dE = 0 \qquad (8)$$

This can be re-arranged to derive the rate of change of the bottom of the valence band with temperature for the metal:

$$\frac{dV}{dT} = -\frac{\int_0^\infty DoS(E)\left\{\frac{\partial P}{\partial E_0}\frac{dE_0}{dT}+\frac{\partial P}{\partial T}\right\}\sqrt{E}\ dE}{\int_0^\infty DoS(E)\frac{\partial P}{\partial E}\sqrt{E}\ dE} \qquad (9)$$

The Fermi function P can be differentiated to determine the partial differentials in Eq. (9):

$$P = \frac{1}{e^{(E-E_0)/kT}+1}$$

$$\therefore \frac{\partial P}{\partial Eo} = \left[e^{(E-E_0)/kT}+1\right]^{-2}e^{(E-E_0)/kT}\frac{-1}{kT} \qquad (10)$$

$$\frac{\partial P}{\partial T} = \left[e^{(E-E_0)/kT}+1\right]^{-2}e^{(E-E_0)/kT}\frac{(E-E_0)}{k}\frac{-1}{T^2}$$

$$\frac{\partial P}{\partial E} = \left[e^{(E-E_0)/kT}+1\right]^{-2}e^{(E-E_0)/kT}\frac{1}{kT} = -\frac{\partial P}{\partial E_0}$$

Substituting into Eq. (9) and re-arranging, we get:

$$\frac{dV}{dT} = \frac{dE_0}{dT} - \frac{\int_0^\infty DoS(E)\left[e^{(E-E_0)/kT}+1\right]^{-2}e^{(E-E_0)/kT}\frac{(E-E_0)}{k}\frac{-1}{T^2}\sqrt{E}\ dE}{\int_0^\infty DoS(E)\left[e^{(E-E_0)/kT}+1\right]^{-2}e^{(E-E_0)/kT}\frac{1}{kT}\sqrt{E}\ dE} \qquad (11)$$

Now, the contribution to the circuit EMF is the change in Fermi Energy per unit charge and the rate of change of the Fermi Energy per unit charge with temperature is given by:

$$\frac{d\,EMF}{dT} = \frac{1}{e}\left(\frac{dV}{dT}-\frac{dE_0}{dT}\right) \qquad (12)$$

From Eq. (11), this can be seen to be:

$$\frac{d\,EMF}{dT} = \frac{\int_0^\infty DoS(E)\left[e^{(E-Eo)/kT}+1\right]^{-2}e^{(E-Eo)/kT}(E-E_O)\sqrt{E}\ dE}{eT\int_0^\infty DoS(E)\left[e^{(E-Eo)/kT}+1\right]^{-2}e^{(E-Eo)/kT}\sqrt{E}\ dE} \qquad (13)$$

Eq. (13) is the contribution of the thermocouple wires to the absolute Seebeck coefficient for a given material. This was evaluated over a range of temperature from 273 K to 373 K using the DoS data sets for platinum and gold by numerical integration. The difference between these Seebeck coefficients was than integrated numerically to arrive at the contribution to the EMF for the gold versus platinum thermocouple:
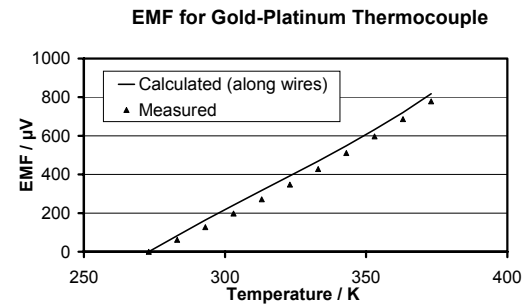
EMF for Gold-Platinum Thermocouple

FIGURE 7: Calculated and Measured EMF for Gold Platinum Thermocouple.

4.2 EMF at the Contacts

The established view is that the thermocouple EMF is generated as a voltage gradient along the thermocouple wires caused by the temperature gradient they experience and that the junctions do not contribute to the measured EMF [5]. This model does not support that view; rather it predicts that there will in general be a small difference in the Fermi Energy and that this will depend on the variation of the DoS for each metal near the Fermi Energy.

The equilibrium condition developed in Eq. (4) can be used to calculate the contribution of the junctions to the measured EMF. In practical measurement situations there would be no significant temperature gradient across the junction so that $T_A=T_B=T$ in Eq. (4). The EMF contribution was determined numerically by evaluating Eq. (4) and iterating δV until both sides of the equation were the same. However, the results predict large values that do not agree with the measured values (-11.54 mV at 100 °C compared with a measured value of $+0.778$ mV).

4.3 Accuracy of the Model

Over the range of the calculations, the model predicts that the temperature gradient along the wires will generate an EMF that is close (within 5 %) to the measured value. There remains, however, a significant discrepancy. The model does not predict the expected low contribution to the EMF of the junctions. An examination of the equations used in the model reveals that these discrepancies are probably due to inadequate resolution in the numeric integration used in the model.

The exponential terms in equation (13) can be re-arranged into the same $P(1-P)$ form found in Eq. (4). The $P(1-P)\sqrt{E}$ components in these two equations are convolved with the DoS data in the integrals and act to 'select' out a narrow region of the DoS functions:

P(1-P)√E and DoS Functions
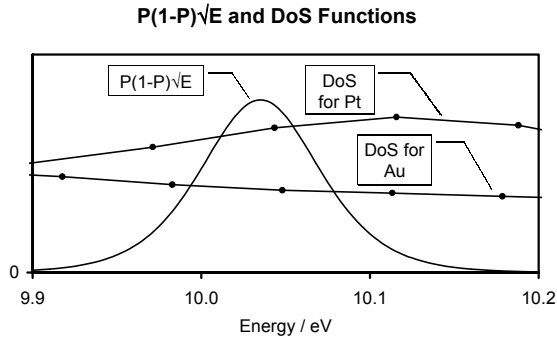
FIGURE 8: Terms in Equilibrium and EMF Equations.

From Figure 8 it is clear that the quantisation of energy for the DoS function is low compared with the required resolution of the calculation; there are only three data points in a 300 mV range used to calculate EMFs that are less than 1 mV. This may account for the discrepancies between the predicted and measured EMF values.

An examination of the propagation of these errors through the calculations reveals that the effect on the calculated EMF along the wires is small (proportional to the error in the integral). However, the effect of the calculated EMF at the junctions is much higher since the re-adjustment required to 'balance' both sides of Eq. (4) with the error included is relatively large. The accuracy of the model could be improved by increasing the resolution of the DoS data sets for gold and platinum around the Fermi Energy.

6. CONCLUSIONS

If the established view that the junctions do not contribute significantly to the EMF is accepted, the model developed and described in this paper predicts the EMF for the gold versus platinum thermocouple within 5 % of the measured value over the range 0 to 100 °C. The model does not predict that the contribution of the junctions to the measured EMF is small as expected. The model's accuracy appears to be compromised by inadequate resolution in the numerical modeling used. The model could be improved by selectively increasing the resolution near to the Fermi Energy in the future. Such improvements will require access to greater computing power than has been used in this work.

Further work is required to develop and validate this model. However, the authors are satisfied that the model provides the basis of a calculable link between thermocouple EMFs and absolute temperature.

ACKNOWLEDGEMENTS

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