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Partial molar entropy of electrons in a jellium model: Implications for thermodynamics of ions in solution and electrons in metals☆

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ABSTRACT

A universal relationship between the partial molar entropy of electrons in a conductor and the absolute thermoelectric power of the conductor was previously established using macroscopic thermodynamics. This relationship may depend on temperature but not on the type of material. Building on this, a recent comment published in this journal, as well as some earlier work, has argued that the partial molar entropy of electrons in a conductor is essentially equivalent to the absolute thermoelectric power of the metal. The argument was based on the thermodynamic and transport properties of a free electron Fermi gas. To further validate the relationship the present paper extends this approach to a jellium model of electronic structure. If the proposed equivalence between partial molar entropy and absolute thermoelectric power is valid it opens the way for an experimental thermodynamic method to measure quantities that have previously been considered un-measurable, such as partial molar entropies of ions in solution and electric fields in homogeneous conductors placed in a temperature gradient. It also relates to questions about the completeness of current thermodynamic theory and the possibility of a new principle or law of thermodynamics.

1. Introduction

An earlier paper in this journal discussed thermoelectrochemical effects and also examined the relationship between the partial molar entropy of electrons in metals and the absolute Seebeck coefficient of the metal, also known as the absolute thermoelectric power [1]. By applying microscopic theory to the problem it was argued that the partial molar electronic entropy and the absolute thermoelectric power are essentially equivalent for all isotropic materials.

Stated briefly, the argument for the validity this proposal uses Eq. (1)

$$G(T) = S + F\sigma \tag{1}$$

where S is the partial molar entropy of electrons in the metal, F is Faraday's constant, and σ is the absolute Seebeck coefficient of the metal. In this equation $G(T)$ is a universal function, i.e. the same for all materials. In the limit of infinite number density both S and σ become zero for a degenerate free electron Fermi gas. This implies that $G(T)$ is also zero. Since $G(T)$ is a universal function, if $G(T)$ must be zero for one isotropic material it is true for all isotropic materials, and one concludes that

$$S = -F\sigma \tag{2}$$

for all isotropic materials. In plain language this relationship means that the partial molar entropy of electrons in a metal is essentially equivalent to the absolute Seebeck coefficient of the metal.

Earlier work also concluded that the partial molar entropy of the electron and the absolute thermoelectric power are essentially equivalent [2,3]. The restriction to isotropic materials has been discussed by Tykodi [2].

As noted above, the relationship summarized in Eq. (2) was derived by considering the thermodynamic properties of a free electron Fermi gas. However, it is good practice to validate a scientific result using more than one line of evidence. Therefore, the present paper takes this analysis one step further to consider the jellium model of electronic structure, which is more similar to a real metal than the free electron model. The jellium model answers certain objections that could be raised against the free electron Fermi gas model.

2. Theoretical development

Because $G(T)$ is a universal function for all materials, the question of whether a particular method of evaluating $G(T)$ is valid or not depends, in part, on what one means by the term "material".

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If one is using a theoretical construct for the test material then an important question is whether the theoretical material has properties that are sufficiently similar to real materials to consider the material as a valid test case. For example, if the argument from Ref. [1] for Eq. (2) of the present paper were to fail, it would be because the physical model upon which it was built (a strongly degenerate free electron Fermi gas) had somehow failed to capture some essential feature of real materials.

The free electron Fermi gas differs from real conductors in several respects. (1) It does not include electron–phonon interactions. (2) It does not include interactions of electrons with a periodic lattice. (3) It does not include electron–electron interactions.

Although some investigators may consider that an analysis of the problem based on the free electron Fermi gas is sufficient to validate Eq. (2), (the present author included,) for other investigators the differences between the free electron gas model and real materials could open objections to using this model to validate Eq. (2). In particular one could ask "Is the degenerate free electron Fermi gas similar enough to real materials to be used to validate Eq. (2)?" Therefore, let us examine the three issues above, starting with electron–phonon interactions.

It is well known that acoustic properties and electronic structure vary between one material and another. Clearly, electron–phonon coupling must therefore vary between one material and another, and since $G(T)$ does not depend on the material, it must mean that $G(T)$ does not depend on electron–phonon interactions.

Next, let us consider the interactions of electrons with a periodic lattice. Lattice properties vary greatly from one conductor to another. Some conductors, such as liquid metals, do not even have a periodic lattice. Therefore, $G(T)$ cannot depend on lattice periodicity.

There is still the possibility that $G(T)$ could depend, in a general way, on the existence of a background of positive charge which interacts with the electrons, even if lattice periodicity is not a factor. Therefore, if one is to go beyond the free electron Fermi gas model to validate Eq. (2) one should use a model in which electrons interact with a background of positive charge. One should also include electron–electron interactions. The simplest system which includes these interactions is the uniform electron gas model, also known as the jellium model. In this model electrons interact with each other as well as a uniformly distributed positive charge.

The thermodynamics of this model can be analyzed in the light of a landmark paper by Kohn and Sham [4]. That paper builds upon earlier results from Hohenberg and Kohn [5] to derive a set of equations they describe as a Hartree–Fock method, corrected for correlation effects, and applies these results, together with a finite temperature generalization from Mermin [6] to analyze the thermodynamics of an interacting Fermi gas. In Section 3 of [4] the authors show that within the approximations employed in their paper the thermodynamics of an electron gas in a potential $v(r)$ can be treated in much the same way as a free particle system in an effective potential shifted relative to that of a free particle system of the same number density.

At high number density the energy per electron of a homogeneous electron gas in the ground state is given by:

$$E = \frac{A_F}{r_s^2} - \frac{B_E}{r_s} + C_C \ln(r_s) - D_C \tag{3}$$

where the term containing A_F is the energy of a degenerate free electron gas, the term containing B_E is the exchange energy, the terms containing C_C and D_C represent the correlation energy, and r_s is the Wigner–Seitz radius, which in the case of a jellium is the radius of a sphere whose volume is equal to the mean volume per electron. In atomic units, A_F and B_E have values of 2.21 and 0.916 respectively. The value of C_C is variously quoted as 0.0313 or 0.0622, depending on the source, and the value of D_C is variously quoted as 0.115 or 0.096, depending on the source [7–10].

If N is the total number of electrons then the total energy of the ground state is

$$E_{Total} = \frac{NA_F}{r_s^2} - \frac{NB_E}{r_s} + NC_C \ln(r_s) - ND_C \tag{4}$$

Considering the relationship between the Wigner–Seitz radius, particle number, and volume

$$\frac{4\pi}{3} r_s^3 = \frac{V}{N} \tag{5}$$

one can re-write the total energy as

$$E_{Total} = N^{5/3} A_F \left(\frac{3V}{4\pi}\right)^{-2/3} - N^{4/3} B_E \left(\frac{3V}{4\pi}\right)^{-1/3} + NC_C \ln\left(\left(\frac{3V}{4\pi N}\right)^{1/3}\right) - ND_C \tag{6}$$

Assuming that V is constant, the Fermi level at 0 K is

$$\mu_{T=0} = \frac{\partial E_{total}}{\partial N} \tag{7}$$

$$\mu_{T=0} = \frac{5}{3} N^{2/3} A_F \left(\frac{3V}{4\pi}\right)^{-2/3} - \frac{4}{3} N^{1/3} B_E \left(\frac{3V}{4\pi}\right)^{-1/3} + C_c \ln\left(\left(\frac{3V}{4\pi N}\right)^{1/3}\right) - \left(\frac{C_C}{3} + D_C\right) \tag{8}$$

$$\mu_{T=0} = \frac{5A_F}{3r_s^2} - \frac{4B_E}{3r_s} + C_c \ln(r_s) - \left(\frac{C_C}{3} + D_C\right) \tag{9}$$

The functional form of this expression is similar to that of the energy per electron (Eq. (3)) but with different constants. For example, it uses $5A_F/3$ in place of A_F. The leading term in Eqs. (8) and (9) is the zero temperature Fermi level of the degenerate free electron Fermi gas. One can see by inspection that as r_s approaches zero the free particle term dominates, and the other terms become negligible by comparison.

Given the fact that the electron density in a jellium is uniform, it seems reasonable to assume that the exchange and correlation energies of low-lying excited states should not be greatly different from those of the ground state. If this were strictly true, then the energy level spacing would be the same as the free particle spacing at the same density. In this case the density of states (which is inversely proportional to the energy level spacing) will show the same limiting form as the density of states of the free electron Fermi gas, and the analysis in Ref. [1] applies, leading to the same conclusion as before, namely that Eq. (2) of the present paper is valid.

Taking a different approach for estimating the density of states near the zero-temperature Fermi level, assume that the energy of promoting an electron from the highest occupied orbital (the zero temperature Fermi level) to the lowest unoccupied level is the same as the difference in energy between an N electron jellium and an $N+1$ electron jellium. This naïve assumption probably not strictly valid, but let us see where it leads

$$\Delta E_{N,N+1} = E_{Total,N+1} - E_{Total,N} = \sim \frac{\partial \mu_{T=0}}{\partial N} \tag{10}$$

$$\frac{\partial \mu_{T=0}}{\partial N} = \frac{10A_F}{9r_s^2 N} - \frac{4B_E}{9r_s N} - \frac{C_C}{3N} \tag{11}$$