

## AN ABSTRACT OF THE THESIS OF

Dara L. Easley for the degree of Master of Science in Physics presented on December 6, 2004.

Title: Seebeck Coefficient in the High Temperature Limit.

Abstract approved:

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Allen L. Wasserman

The Seebeck coefficient is examined in the high temperature limit, using an approach based on a grand partition function containing Hubbard Hamiltonian interaction terms. Although the carriers of interest occupy localized Wannier states, this work is prefaced by the case of delocalized Bloch states, which is examined using Boltzmann transport, and yields the Seebeck coefficient in the free-particle limit. Transfer matrix methods are used to consider both on-site and nearest-neighbor interactions for a Hubbard chain. Examination of results in limiting cases, specifically those of zero or infinite interactions, agree with those calculated in literature using a combinatoric approach. The least-bias approach is applied to the two-atom system for the case of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ . Results are in reasonable agreement with the experimental Seebeck data for this material. It is determined that the double occupancy term in the grand partition function dominates any single occupancy contribution, thus the theoretical result for the temperature-dependent Seebeck coefficient for this system is a function of an intercalated atom concentration term,  $\rho$ , and a binding energy parameter,  $\epsilon$ , for sites on oxygen atoms. Comparison to experimental data demonstrates that  $\epsilon$  decreases as  $\rho$  increases, suggesting the formation of an oxygen band. Langmuir's model of surface adsorption is applied to the copper layer, treating this as a copper surface to which a free gas, oxygen, is adsorbed. Analysis using this model verifies the correlation between the oxygen pressure at which the samples are intercalated and the intercalated atom (oxygen) concentration. This conclusion provides a context for interpreting  $\rho$  that originated in the least-biased approach.

Seebeck Coefficient in the High Temperature Limit

by  
Dara L. Easley

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Dara L. Easley, Author

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# 1 INTRODUCTION

## 1.1 Problem Definition

The discovery in 1821 that a thermal gradient created across a material could generate a measurable voltage was followed by immediate interest in the topic. This interest in thermoelectrics waned after thirty years, and the practical applications resulting from this effect remained largely unexplored until the 1930s [1]. At this time, the interest in thermoelectric (TE) materials revived, and has continued to grow steadily until 1970 [1]. A more recent second revival of TEs accompanies the growth of materials science and the semiconductor industry. In comparison to metallic thermocouples which generate relatively small voltages, thermocouples made from semiconducting materials produce much larger voltages and in principle can convert heat directly to electricity, or vice versa, thus acting as TE coolers and heaters, respectively [2].

The problem with current TE materials is low efficiency, making these materials impractical for industry or even consumer use. The performance of TE materials is characterized by a figure of merit,  $ZT$ , where  $Z$  is the material coefficient and  $T$  is the temperature. An interesting characteristic of this figure of merit is that it has no apparent thermodynamic upper limit [3]. TE power generation devices using TE materials with  $ZT < 1$  correspond to a Carnot efficiency of less than 30% of the Carnot limit [1]. Thus, ideal TE materials maximize this figure of merit. The figure of merit is directly proportional to the square of the Seebeck coefficient, which will be described in detail later in this paper. Therefore, one desirable characteristic of TE materials is a large Seebeck coefficient.

The Seebeck coefficient is a fundamentally complex problem since it depends on both kinetic carrier movement and the equilibrium entropy. In addition to the carrier movement mechanism, which is determined by the kinetics of carrier scattering or local site-to-site kinetics (hopping), other factors such as phonons may influence a

carrier's movement. These phonons are coupled to the electron via scattering kinetics, i.e. phonon drag. Electron-phonon coupling is a complex interaction that is outside the scope of this paper. However, the hopping transport mechanism and its effect on the Seebeck coefficient will be examined in more detail in the discussion on heat transfer.

## 1.2 Motivation

The characterization of new TE materials by a figure of merit that is strongly dependent on the Seebeck coefficient has renewed an interest in understanding the Seebeck coefficient from a first principles perspective. The materials science community must understand the Seebeck coefficient at a fundamental level in order to succeed in maximizing it. Additionally, current research in p-type transparent conductive oxides has influenced this project. Some of these materials, such as  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  thin films, exhibit hopping as the carrier transport mechanism [4]. This encouraged the examination of the Seebeck coefficient not only in the hopping regime, but also in the high temperature limit, where a useful simplification can be made. Furthermore, the desire to determine material parameters such as carrier concentration from experimental data for materials such as  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  is another motivation for this project.

## 1.3 Statement of Purpose

The objective of this project is twofold. First, a detailed understanding of the Seebeck coefficient is necessary. Thus, a thorough review of many existing derivations of the Seebeck coefficient is completed, followed by a comprehensive derivation from a first principles approach. The second aspect of this project is to examine the Seebeck coefficient in the high-temperature hopping regime using a model based on physical parameters, and to compare these results to those discussed in existing literature which take a less physical approach that emphasizes statistical and combinatoric methods. An additional emphasis is taken in this paper to make the discussions applicable for

both types of charge carriers, namely holes and electrons. Thus, formulae in this paper are generalized for a carrier with charge  $q$ .

#### 1.4 Overview of this Thesis

This thesis begins with a discussion of the mechanisms that influence the transfer of heat within a material. The Seebeck coefficient is then briefly introduced from a familiar thermocouple perspective, and the details of this engineering approach are provided in Appendices A and B. This discussion is followed by an introduction of the Seebeck coefficient from a chemical potential perspective (entropy “current”). In Section 2.4, a first principles derivation of the Seebeck coefficient is completed; this derivation is essential for all calculations to follow. Section 2.5 illustrates a calculation of the Seebeck coefficient using Boltzmann transport theory. Although this approach is only valid for delocalized Bloch states, this calculation is worthwhile because it uses familiar Boltzmann theory (described in more detail in Appendix C) and yields the free-particle limit of the formula presented in the papers examined for the literature review.

Chapter 3 examines the Seebeck coefficient in the high temperature, hopping regime. This chapter also contains the literature review of a paper that presents a theoretical approach to the Seebeck coefficient by examining possible carrier configurations on lattice sites. Results from this paper are presented, and will be referenced for comparison in Chapters 4 and 5. This paper also introduces the significance of the Hubbard Hamiltonian to the Seebeck coefficient in the high temperature, hopping regime.

Chapter 4 introduces the least-bias approach to calculating the Seebeck coefficient. This approach uses the grand partition function, containing Hubbard Hamiltonian interaction terms, to calculate the chemical potential and ultimately the Seebeck

coefficient. Calculations using this approach, and results from comparisons with those from the literature review in Chapter 3, are included in Section 4.4 of this chapter. This chapter closes with a discussion of the results.

Chapter 5 discusses the transfer matrix approach, another method for determining the grand partition function necessary for completion of the least-biased approach. This method utilizes the fundamentals of the Ising Model, which is described briefly in Appendix E. Section 5.3 shows the calculations and results for the transfer matrix approach. The advantages and disadvantages of this approach are included with a discussion of the results in Section 5.4.

Chapter 6 discusses an application of the least-biased approach for calculating the Seebeck coefficient in the high-temperature regime for narrow-band materials with hopping carriers, the two-atom system. A specific case of the material  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  is considered. Information on this material necessary for applying the least-biased approach correctly is given in Section 6.2. Calculations for this case are given in Section 6.3 and Appendix F. Results are presented at the end of the chapter and compared to experimental temperature-dependent Seebeck data for  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ . This comparison shows that the theoretical result compares reasonably well with the experimental data. The chapter ends with a discussion of these results.

The final chapter of this thesis, Chapter 7, gives a conclusion of the work done within this thesis and a brief summary of results.

## **2 GENERAL SEEBECK THEORY**

### **2.1 Heat Transfer**

There are two mechanisms that contribute to heat transfer within a material. The first is the transport of heat by charge carriers, the mechanism that causes metallic materials with larger electrical conductivities than other materials to be good conductors of heat [1]. However, the fact that heat can also be transported in insulators, which are characterized by small electrical conductivities, suggests that this is not the only mechanism present. The second mechanism at work is the transfer of vibrational energy from one atom to the next [1]. Since the atoms in a crystalline material are part of a bigger structure, a lattice, we can no longer think of the atoms as independent. Thus, it is the lattice structure, not individual atoms, that responds to incident vibrational waves. The boundary conditions, caused by the discrete nature of the atoms, put constraints on the types of waves allowed within the structure [1]. It was Peierls who introduced the concept of “phonon” wave packets that arise from the quantization of vibrational waves to explain this process [1]. These wave packets are now just referred to as phonons, and can be thought of as “the energy carriers that are responsible for the heat conduction by a lattice” [1]. The phenomenon called phonon drag that complicates the Seebeck effect is precisely the interaction of these heat-current carrying phonons that have been scattered by the conduction carriers [1].

### **2.2 Seebeck Introduction**

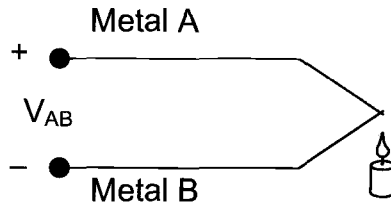
Many texts introduce Seebeck, or thermopower, theory and the resulting Seebeck coefficient from an engineering perspective, using thermocouple theory. This will briefly be presented in this section, with supporting information in the appendices. However, the thermocouple explanation provides a limited insight into the physical processes taking place in the sample. Thus, a derivation of the Seebeck coefficient from a first principles perspective will also be presented in this chapter. The first

principles derivation is essential for the high temperature discussion and approximation presented in the following chapter.

## 2.3 Seebeck Theory

### 2.3.1 Open circuit analysis

A thermocouple is a device used for measuring temperature that is made up of two dissimilar metals joined at one end [5]. The thermocouple junction is heated while the open ends are held at a constant reference temperature and a thermoelectric voltage can be measured across the open ends, as shown by the open circuit in Figure 2.1.



**Figure 2.1 Seebeck voltage, thermocouple**

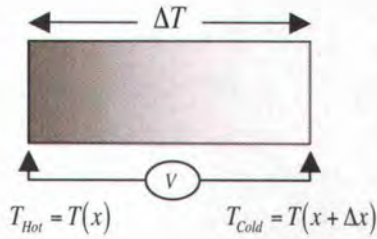
For small differences in temperature, the Seebeck voltage is directly proportional to the temperature difference [5], as shown by

$$V_{AB} = \alpha \Delta T. \quad (2.1)$$

Here,  $V_{AB}$  is the measured Seebeck voltage,  $\Delta T$  is the temperature difference between the junction and the open ends, and the coefficient of proportionality,  $\alpha$ , is the Seebeck coefficient characteristic of the metal pair.

### 2.3.2 Seebeck effect in a single homogeneous material

In theory, a Seebeck voltage exists across any sample of material with a temperature difference maintained at the ends, as shown in Figure 2.2.



**Figure 2.2 Seebeck voltage, material**

In practice, any resistance in the leads attached to a voltmeter will affect the measured Seebeck voltage. This must be accounted for in calculations using (2.1). For the moment, this detail will be disregarded.

The nature of the thermoelectric effect within a material is typically explained using classical diffusion and energy arguments. Since this is the explanation most commonly found in textbooks, I have included a discussion from this view in Appendix A and the necessary differential thermocouple theory in Appendix B. However, the Seebeck effect is fundamentally a chemical potential problem, as demonstrated by the thermodynamic approach involving the partition function, described later in this paper. Thus, I will begin here with a chemical potential description of the Seebeck effect.

### 2.3.3 Seebeck effect and its relationship to the chemical potential

The chemical potential,  $\mu$ , is a thermodynamic property of the carriers within a material and it is related to thermodynamic variables such as internal energy by means of the First Law of Thermodynamics,

$$dU = Td\zeta - PdV + \mu dN. \quad (2.2)$$

Here,  $U$ ,  $\zeta$ ,  $V$  and  $N$  are the internal energy, entropy, volume and number of particles, respectively. Solving (2.2) for the chemical potential in terms of energy illustrates how the chemical potential can be thought of as “energy” per particle,



$$\mu = \left( \frac{dU}{dN} \right)_{\epsilon, V}. \quad (2.3)$$

Equivalently, one could solve (2.2) for the chemical potential in terms of entropy, illustrating how the chemical potential could also be thought of as “entropy” per particle.

$$\mu = - \left( \frac{d\zeta}{dN} \right)_{U, V}. \quad (2.4)$$

The chemical potential is also often described by its relationship to the electrochemical potential energy, namely

$$\bar{\mu} = \mu + q\Phi. \quad (2.5)$$

Here,  $\bar{\mu}$  and  $\Phi$  are the electrochemical potential energy and the electrostatic potential [6], respectively, and  $q$  is the charge of carrier including the sign ( $q = -|e|$  for electrons,  $q = |e|$  for holes).

Since there is a temperature gradient across the material shown in Figure 2.2, a gradient in the chemical potential is also present because the chemical potential is temperature dependent. The Seebeck coefficient,  $S$ , ultimately describes this infinitesimal change in chemical potential per change in temperature, and can be written as

$$S = - \frac{1}{q} \frac{\partial \mu}{\partial T}. \quad (2.6)$$

This expression will be derived from a first principles argument in the following section.

The Seebeck coefficient is usually given in units  $\mu V/K$  (microvolts per Kelvin). Thus, the term “thermoelectric power” or “thermopower” is misleading, because the

coefficient is by no means power. An important characteristic of the Seebeck coefficient is that the sign of the coefficient corresponds to the type of charge carrier present in the material. Thus, the Seebeck coefficient is positive if the carriers are holes and negative if the carriers are electrons. For semiconducting materials this would correspond to p-type and n-type materials, respectively. This is seen by examining (2.6) for fermions, where by definition  $\partial\mu/\partial T < 0$ ; for electrons,  $q = |e|$  yielding  $S < 0$ , and for holes  $q = |e|$  yielding  $S > 0$ .

## 2.4 Seebeck Theory, First Principles Approach

### 2.4.1 Motivation

Although the qualitative description of the Seebeck effect presented earlier, and that of carrier movement presented in Appendix A, are useful, they should be accompanied by a detailed quantitative derivation. Thus, a first principles approach to the Seebeck coefficient is presented in the following section.

### 2.4.2 Deriving a meaningful formula for the Seebeck coefficient

The physical condition of dynamic equilibrium that characterizes the Seebeck effect is that heat is transferred through the sample without the actual transfer of charge, when a small temperature gradient exists across a material. Thus, to calculate the Seebeck coefficient, one can compute the gradient of the electrochemical potential needed to offset the current flow [7]. This can be examined by setting the charge current density,  $\mathbf{J}$ , given by

$$\mathbf{J} = q\mathbf{I}, \quad (2.7)$$

to zero. Here,  $\mathbf{I}$  is the carrier density described by the Onsager transport equation [8] given by

$$\mathbf{I} = -\frac{\sigma}{q^2} \nabla \bar{\mu} - \frac{S\sigma}{q} \nabla T. \quad (2.8)$$

Here,  $\sigma$  is the electrical conductivity of the material,  $\bar{\mu}$  is the electrochemical potential,  $T$  is the temperature, and  $S$  is the Seebeck coefficient.

Substituting (2.8) into (2.7), and setting  $\mathbf{J}$  in (2.7) equal to zero, to represent no current transport within the sample, yields

$$\frac{\sigma}{q} \nabla \bar{\mu} = -S \sigma \nabla T. \quad (2.9)$$

The electrochemical potential energy,  $\bar{\mu}$ , is comprised of the chemical potential,  $\mu$ , and electrostatic potential,  $\Phi$ , as given by (2.5). Since no external voltage is applied to the sample for the Seebeck effect,  $\Phi = 0$ , the gradient of the electrochemical potential in (2.9) reduces to the gradient of the chemical potential,  $\bar{\mu}(\Phi = 0) = \mu$ ,

$$\frac{\sigma}{q} \nabla \mu = -S \sigma \nabla T. \quad (2.10)$$

Considering, for example, transport in only the  $x$ -direction, the following substitution is made,

$$\begin{aligned} \nabla \mu &\rightarrow \frac{\partial \mu}{\partial x} \hat{x} \\ \nabla T &\rightarrow \frac{\partial T}{\partial x} \hat{x} \end{aligned} \quad (2.11)$$

Solving (2.10) for  $S$  and applying (2.11) yields our first fundamental description of the Seebeck coefficient,

$$S = -\frac{1}{q} \left( \frac{\partial \mu}{\partial T} \right). \quad (2.12)$$

## 2.5 Calculating the theoretical Seebeck coefficient

One way to determine an expression for (2.12) is to examine Boltzmann transport theory combined with band theory. Although this only holds for delocalized Bloch states (free carriers that scatter), and we are ultimately interested in the case of localized Wannier states (bound carriers that hop), it nonetheless provides a starting point and a straightforward approach for the form of the Seebeck coefficient.

Non-equilibrium carriers of a system are typically described by a local occupation function,  $f(\mathbf{r}, \mathbf{k}, t)$ , which is a solution to Boltzmann's transport equation. Here,  $\mathbf{r}$  is the local spatial coordinate,  $\mathbf{k}$  is the wavenumber of a quantum state and  $t$  is an explicit time dependence. Since holes and electrons are fermions, in equilibrium the distribution for either carrier type is given by the Fermi distribution function,

$$f_o(\epsilon) = \frac{1}{1 + e^{\beta(\epsilon - \mu)}}. \quad (2.13)$$

Here,  $\epsilon$  is the energy of the carrier. In the Boltzmann picture, the energy for electrons and holes is  $\epsilon = \hbar^2 k^2 / 2m$  and  $\epsilon = -\hbar^2 k^2 / 2m$ , respectively. Sommerfeld determined that the number of carrier states permitted per unit volume within a defined energy range from  $\epsilon$  to  $\epsilon + d\epsilon$  is given by [1,9]

$$g(\epsilon)d\epsilon = \frac{4\pi(2m)^{3/2} \epsilon^{1/2} d\epsilon}{h^3}. \quad (2.14)$$

Here,  $g(\epsilon)$  is the free particle density of states. Thus, the number of charge carriers per unit volume in the aforementioned energy range is described by

$$f(\epsilon)g(\epsilon)d\epsilon. \quad (2.15)$$

Reducing the problem to one dimension defines carriers of charge  $q$  as moving in the  $x$  direction with a velocity  $v_x$ . Then the current per area, or electric current density  $j$  [1], is given by

$$j = \int_0^{\infty} qv_x f(\epsilon) g(\epsilon) d\epsilon. \quad (2.16)$$

No net charge flows when the system is in equilibrium described by (2.13). Thus, when  $f(\epsilon) = f_o(\epsilon)$ , the current, and thus the current density, must be zero [1]. Therefore, (2.16) is modified to include this constraint, and the current density is rewritten as

$$j = \int_0^{\infty} qv_x (f(\epsilon) - f_o(\epsilon)) g(\epsilon) d\epsilon. \quad (2.17)$$

Next, Boltzmann's transport theory in the relaxation time approximation is used to determine  $f(\epsilon) - f_o(\epsilon)$ . Boltzmann's transport equation, given by

$$\frac{f(\epsilon) - f_o(\epsilon)}{\tau} = v_x \frac{\partial f_o}{\partial \epsilon} \left( \frac{(\epsilon - \mu)}{T} \frac{\partial T}{\partial x} + \frac{\partial \mu}{\partial x} \right), \quad (2.18)$$

is derived in Appendix C. Here,  $\tau$  represents the scattering time, which is the time duration between scattering events. For details, see Appendix C.

Solving (2.18) for  $f(\epsilon) - f_o(\epsilon)$ , the current density, given by (2.17), is rewritten and simplified as follows,

$$j = \int_0^{\infty} qv_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \left( \frac{(\epsilon - \mu)}{T} \frac{\partial T}{\partial x} + \frac{\partial \mu}{\partial x} \right) g(\epsilon) d\epsilon. \quad (2.19)$$

Applying the condition that  $j = 0$  in dynamic equilibrium, which is a characteristic of the Seebeck effect discussed earlier in the first principles derivation, one can solve for  $\partial \mu / \partial T$  needed in equation (2.12). This solution method is demonstrated in the following equations,

$$\int_0^{\infty} qv_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \frac{(\epsilon - \mu)}{T} \frac{\partial T}{\partial x} g(\epsilon) d\epsilon = - \int_0^{\infty} qv_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \frac{\partial \mu}{\partial x} g(\epsilon) d\epsilon \quad (2.20)$$

$$\frac{1}{T} \frac{\partial T}{\partial x} \int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} (\epsilon - \mu) g(\epsilon) d\epsilon = - \frac{\partial \mu}{\partial x} \int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon \quad (2.21)$$

$$\frac{\partial \mu}{\partial x} = - \frac{\frac{1}{T} \frac{\partial T}{\partial x} \int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} (\epsilon - \mu) g(\epsilon) d\epsilon}{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon} \quad (2.22)$$

$$\frac{\partial \mu}{\partial x} = - \frac{1}{T} \frac{\partial T}{\partial x} \left( \frac{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \epsilon g(\epsilon) d\epsilon - \mu \int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon}{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon} \right) \quad (2.23)$$

$$\frac{\partial \mu}{\partial x} = - \frac{1}{T} \frac{\partial T}{\partial x} \left( \frac{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \epsilon g(\epsilon) d\epsilon}{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon} - \frac{\mu \int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon}{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon} \right) \quad (2.24)$$

$$\frac{\partial \mu}{\partial x} = \frac{1}{T} \frac{\partial T}{\partial x} \left( \mu - \frac{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \epsilon g(\epsilon) d\epsilon}{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon} \right) \quad (2.25)$$

$$\frac{\partial \mu}{\partial T} = \frac{\partial \mu}{\partial x} \frac{\partial x}{\partial T} = \frac{1}{T} \left( \mu - \frac{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \epsilon g(\epsilon) d\epsilon}{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon} \right) \quad (2.26)$$

Substituting (2.26) into (2.12) yields the final equation for the Seebeck coefficient based on a first principles derivation,

$$S = - \frac{\mu}{qT} + \frac{\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} \epsilon g(\epsilon) d\epsilon}{T \int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \epsilon} g(\epsilon) d\epsilon}, \quad (2.27)$$

an expression that appears widely in the literature e.g. [10,6]. This can be rewritten as

$$S = -\frac{\mu}{qT} - \frac{K^1/K^0}{T}, \quad (2.28)$$

where  $K^1$  and  $K^0$  are scattering integrals,

$$\begin{aligned} K^1 &= -\int_0^\infty q v_x^2 \tau \frac{\partial f_o}{\partial \varepsilon} \varepsilon g(\varepsilon) d\varepsilon \\ K^0 &= \int_0^\infty q^2 v_x^2 \tau \frac{\partial f_o}{\partial \varepsilon} g(\varepsilon) d\varepsilon \end{aligned} \quad (2.29)$$

### 3 SEEBECK THEORY IN THE HIGH TEMPERATURE, HOPPING REGIME

#### 3.1 Introduction

The derivation of the Seebeck coefficient given by (2.28) is based on Boltzmann transport theory, also called one-electron theory since it describes the response of an independent charge carrier. This is a valid approach for materials with broad bands and where  $\tau \gg 1$ , such as pure metals and defect-free semiconductors. However, a free-electron gas does not provide a good model for the narrow-band materials with localized impurities, where  $\tau \ll 1$ , of interest in this paper. For example, highly-doped materials where the dopants overlapped, creating bands. In 1963, J. Hubbard introduced a “theory of correlations” to examine such systems of interacting carriers in a crystal lattice [11,12] for which Bloch states are no longer a good representation. Hubbard’s Hamiltonian is widely used to describe the interaction terms for narrow-band materials. It has also been shown that carriers in these semiconductor bands may contribute to conduction by means of thermally activated hopping [13]. The following literature review was performed to examine papers incorporating hopping, and thus the Hubbard Hamiltonian, into thermopower analysis.

#### 3.2 Literature Review

The basis for this section is three sequential papers discussing the use of Hubbard formalism in thermopower calculations [14,15,16]. The first of these presented experimental data and comparisons with previous calculations [14] for quasi one-dimensional systems. The latter two papers [15,16] expand on localized thermopower theory as discussed in further detail in this section.

##### 3.2.1 *Chaikin and Beni*

“Thermopower in the correlated hopping regime” by P. M. Chaikin and G. Beni is motivated by experimental research done on compounds with properties satisfying the narrow-band Hubbard model. Chaikin and Beni begin by using Kubo formalism [15]



to transform the equation for the Seebeck coefficient to a more applicable formula<sup>1</sup> for semiconducting materials, given by

$$S = -\frac{\mu}{qT} - \frac{S^{(2)}/S^{(1)}}{T}. \quad (3.1)$$

Here,  $S^{(1)}$  and  $S^{(2)}$  are transport correlation functions, that represent a carrier velocity term and a heat term, respectively [17]. Also note that (3.1) has a form similar to that of (2.28), which is a special case of the Kubo formalism result, (3.1), representing the free-particle (weak-scattering) limit. Whereas (2.26) is valid only for delocalized Bloch states, (3.1) is generalized to localized (tight-binding) Wannier states. Beni examined the thermopower of narrow-band Hubbard systems two years prior to the aforementioned work with Chaikin, by using perturbation theory to evaluate the correlation functions  $S^{(1)}$  and  $S^{(2)}$  [17]. Since these correlation functions are mathematically complicated, I became particularly interested in the following approach presented by Chaikin and Beni in their 1976 publication. They claim in the high temperature limit, the  $S^{(2)}/S^{(1)}$  term becomes temperature independent, unlike the chemical potential [15]. Thus, as  $T \rightarrow \infty$ , (3.1) reduces to

$$S(T \rightarrow \infty) = -\frac{\mu}{qT}, \quad (3.2)$$

which is not only mathematically more straightforward, but also lends itself to equilibrium thermodynamic analysis.

The chemical potential is contained in the first law of thermodynamics,

$$dU = Td\zeta - PdV + \mu dN. \quad (3.3)$$

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<sup>1</sup> There is a misprint in Chaikin and Beni's publication on page 647 such that this formula appears as  $S = -\frac{S^{(2)}/S^{(1)} + \mu/e}{T}$ . This formula is then corrected on the following page,  $S = -\frac{S^{(2)}/S^{(1)}}{T} + \frac{\mu}{eT}$ . Here,  $e$  is the absolute value of the electron charge. Substituting  $e \rightarrow -q$  in this formula, and in the  $S^{(2)}/S^{(1)}$  terms, yields the form used in this thesis:  $S = -\frac{\mu}{qT} - \frac{S^{(2)}/S^{(1)}}{T}$ .

Here,  $U$ ,  $\zeta$ ,  $V$  and  $N$  are the internal energy, entropy, volume and number of particles, respectively. Note that the chemical potential,  $\mu$ , is proportional to an entropy per carrier at constant internal energy and volume, and is given by

$$\frac{\mu}{T} = - \left( \frac{\partial \zeta}{\partial N} \right)_{U,V}. \quad (3.4)$$

Using (3.4), Chaikin and Beni take a theoretical approach for calculating  $\mu$  by examining possible carrier configurations on the atomic lattice sites. Boltzmann's entropy<sup>1</sup> is given by

$$\zeta = k_B \log g, \quad (3.5)$$

where  $g$  represents a degeneracy or multiplicity function at constant internal energy. Chaikin and Beni then use a combinatorics approach to calculate  $g$  corresponding to different configurations for the carriers on atomic sites. They determine the thermopower, or Seebeck coefficient, in various "regions of applicability," defined by the magnitude of the correlation parameters in the extended Hubbard Hamiltonian, [15]

$$H = -t \sum_{i,\sigma} (C_{i,\sigma}^\dagger C_{i+1,\sigma} + C_{i+1,\sigma}^\dagger C_{i,\sigma}) + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'}. \quad (3.6)$$

Here,  $t$  is the transfer matrix element, also called the nearest-neighbor tight-binding transfer integral;  $C_{i,\sigma}^\dagger$  and  $C_{i,\sigma}$  create and destroy a carrier with spin  $\sigma$  at the  $i$ th site, respectively;  $n_{i,\sigma} = C_{i,\sigma}^\dagger C_{i,\sigma}$  is the number operator for spin  $\sigma$ ;  $U_o$  is the on-site Coulomb interaction and  $U_j$  is the Coulomb interaction between carriers on sites  $j$  units apart [15,16]. All "regions of applicability" explored by Chaikin and Beni are within the limit of a small transfer matrix element,  $k_B T \gg t$ . Since  $t$  arises from a

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<sup>1</sup> Here,  $\log = \log_e$ .

kinetic energy term between neighboring states, the case of small  $t$  corresponds to a nearly static *electrical* state of the system. Note that heat can still be transferred through the system even though charge is not transferred, as discussed in the heat transfer section earlier in this paper.

I will discuss three of the cases presented in Chaikin and Beni's paper, to which I will make comparisons later in this paper.

### 3.2.1.1 Heikes Formula

For this case, the system is described as spinless fermions on atomic sites, where only single occupancy is allowed. The calculated degeneracy for this system is given by

$$g = N_A! / N!(N_A - N)!, \quad (3.7)$$

where  $N$  is the number of electrons and  $N_A$  is the number of atomic sites [15]. They calculate the Seebeck coefficient given by (3.2) using Stirling's approximation, with the result,

$$S(T \rightarrow \infty) \rightarrow -(k_B/e) \ln[(1-\rho)/\rho], \quad (3.8)$$

the so-called Heikes formula. Here,  $\rho = N/N_A$  is the ratio of electrons to sites (carrier concentration) and  $e$  is the absolute charge of an electron [15]. The Seebeck coefficient is usually given in units  $\mu\text{V}/\text{K}$ , and the magnitude of the leading factor  $k_B/e$  is approximately  $86.2\mu\text{V}/\text{K}$ . One of Chaikin and Beni's motivations for their paper was the concern that there was "a great deal of misuse" of the Heikes formula in the analysis of thermopower of narrow-band systems [15]. They predicted the following two cases, presented here in Sections 3.2.1.2 and 3.2.1.3, would be more useful than the Heikes formula.

### 3.2.1.2 Interacting Systems, fermions with spin

In this case, they consider the aforementioned system but allow double-occupancy to be as likely as single-occupancy on a site. They calculate the appropriate degeneracy,

and determine the Seebeck coefficient, [15]

$$S(T \rightarrow \infty) \rightarrow -(k_B/e) \ln[(2 - \rho)/\rho]. \quad (3.9)$$

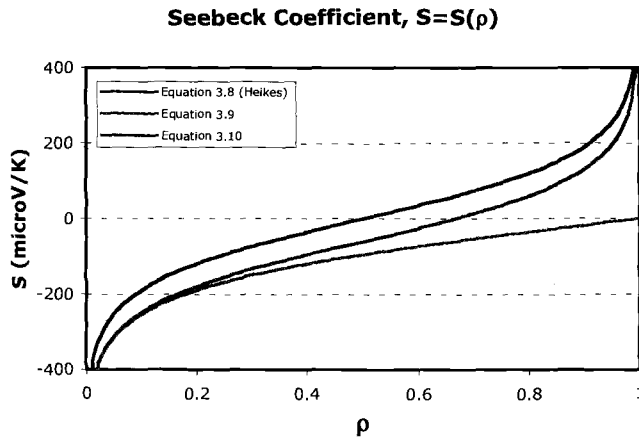
### 3.2.1.3 Interacting Systems, on-site repulsion

This case is also similar to the Heikes case, in that only single occupancy is allowed on an atomic site. However, now spin is taken into account. Chaikin and Beni calculate the Seebeck coefficient, [15]

$$S(T \rightarrow \infty) \rightarrow -(k_B/e) \ln(2[1 - \rho]/\rho). \quad (3.10)$$

### 3.2.2 Discussion

An application of the formulas for the Seebeck coefficient calculated in Chaikin and Beni's paper is determining the carrier concentration,  $\rho$ , using a measured value of the Seebeck coefficient [18]. The three cases examined in Sections 3.2.1.1 – 3.2.1.3 yield different formulas for the Seebeck coefficient and thus fundamentally different trends when examined as a function of  $\rho$ .



**Figure 3.1 Plot of Seebeck coefficient equations (3.8), (3.9) and (3.10)**

Thus, without properly examining the assumptions that influenced (3.8), (3.9) and (3.10), one could potentially incorrectly interpret the carrier concentration from their

physical Seebeck results by applying a formula that is inconsistent with the physical parameters in their material. This is why Chaikin and Beni mentioned in their paper that they believe there is “a great deal of misuse” of the Heikes formula. For example, many publications use (3.8) or (3.10) without extensive arguments discussing the physical applicability of these formulas [10,19,20,21].

There are disadvantages to the approach taken by Chaikin and Beni. The primary disadvantage is that the combinatoric approach for calculating the degeneracy factor examines possible carrier configurations on the atomic sites, making the problem more like the classic statistics problem of  $X$  red balls and  $Y$  black balls, rather than one of physical parameters. The result of their approach is an equation for the Seebeck coefficient that is independent of the Coulomb interaction parameters and temperature. Thus, a motivation for my research is to determine the Seebeck coefficient using a least-biased thermodynamic approach, discussed in the next chapter, such that the result for the Seebeck coefficient will be a function of these and other physical parameters.

## 4 LEAST-BIAS APPROACH

### 4.1 Introduction

A least-bias approach was used to determine the Seebeck coefficient in the high-temperature limit for narrow-band materials with carriers whose transport mechanism is hopping. The objective for this approach is to examine the Seebeck coefficient as a function of concentration, from an equilibrium thermodynamics perspective that preserves microscopic physical information about the system, such as temperature and the Coulomb interaction terms of the Hubbard Hamiltonian. Limiting cases of the Seebeck coefficient solution are also examined for comparison with the results presented in the Chaikin and Beni paper discussed in the literature review in the previous section.

This chapter begins with a general discussion of the least-bias method and how it is applied to the Seebeck problem. Section 4.4 shows the calculations and results for the Seebeck coefficient using this least-bias approach. This chapter closes with a discussion of the results, including how they compare with the results from the Chaikin and Beni paper mentioned in 3.2.1.

### 4.2 Discussion of Method

The least-bias approach incorporates the macroscopic canonical probabilities from statistical mechanics into the method of Lagrange multipliers. The latter method includes terms from an entropy function, which introduces the mixed-state density operator from quantum mechanics. The method of Lagrange multipliers also includes the expectation value of the canonical Hamiltonian, which introduces thermodynamic quantities. Thus, the least-bias approach is inherently a quantum-statistical thermodynamics approach, lending itself to applications in condensed-matter physics.

We begin by treating the material for which we want to examine the Seebeck

coefficient as a quantum system, thus introducing the mixed-state operator. In quantum mechanics, states with maximal information are referred to as pure states. Thus, any state with less information is referred to as a “mixed state” and can be represented by the mixed state density operator,  $\rho_{op}^M$ . The eigenvalues for the mixed state density operator are the probabilities that the system is in a mixed state  $s$  with energy  $E_s$ . Thus, the trace of the mixed state density operator is just the sum of probabilities, and thus must equal one.

The mixed state density operator provides us with information about the system since it can be used to calculate average values, which we know can be related to observable quantities. For example, the internal energy for a system is the expectation value of the Hamiltonian energy operator [22], which can be expressed in terms of the mixed state density operator

$$U = \langle \mathcal{H}_{op} \rangle = \frac{Tr \rho_{op}^M \mathcal{H}_{op}}{Tr \rho_{op}^M}. \quad (4.1)$$

However, in order to apply this to the macroscopic problem of the Seebeck coefficient, we need to introduce thermodynamic theory so that we can calculate the chemical potential. Since we know nothing about the quantum state of the system, we assume the system is in a mixed state with the minimal amount of information, and thus in the state with the least bias.

The method of Lagrange multipliers yields a solution to an optimization problem. More specifically, this method finds the extremal values of a function that is subject to some set of constraints by examining the Lagrangian for the system. By least-bias we mean that we want the most-probable or most-likely case. According to the second law of thermodynamics, the most probable case is that which maximizes the entropy. Thus the function to be maximized within the Lagrangian should be directly related to entropy.

Recall from the discussion of the Chaikin and Beni paper in Chapter 3 of this paper, that Boltzmann's entropy postulate is

$$\zeta = k_B \log g_s. \quad (4.2)$$

Here,  $\zeta$  is the entropy of the  $g_s$ -fold degenerate state with energy  $E_s$ . This expression for Boltzmann's entropy is presented in Chaikin and Beni's paper, however it can be shown that it is a corollary of the least-biased approach as follows. Assuming a system has  $g_s$ -fold degeneracy, let the probability of the  $\gamma^{\text{th}}$  degenerate state be  $\mathcal{P}(E_{s,\gamma})$ . The entropy for the system is then given by

$$\zeta = -k_B \sum_{\gamma=1}^{g_s} \mathcal{P}(E_{s,\gamma}) \log \mathcal{P}(E_{s,\gamma}). \quad (4.3)$$

In order to examine the "least-biased entropy", the least-biased probabilities need to be determined. The least-biased case occurs when all probabilities are equal, i.e. when no particular state is biased. Thus, the least-biased probability for a system with  $g_s$ -fold degeneracy is then  $\mathcal{P}(E_s) = 1/g_s$  for all states  $\gamma$ . The least-biased entropy is then given by

$$\zeta = -k_B \sum_{\gamma=1}^{g_s} \left( \frac{1}{g_s} \right) \log \left( \frac{1}{g_s} \right). \quad (4.4)$$

Since the expression inside the sum is no longer a function of  $\gamma$ , the sum over  $g_s$  states in (4.4) can be simplified,

$$\zeta = -k_B g_s \left[ \left( \frac{1}{g_s} \right) \log \left( \frac{1}{g_s} \right) \right]. \quad (4.5)$$

Further simplification of (4.5) yields

$$\zeta = k_B \log g_s, \quad (4.6)$$

which is precisely Boltzmann's entropy shown in (4.2).



Thus, for a least-biased system, i.e. a system of equally-probable states, the general case of (4.3) is reduced to a special case expressed by the following function

$$\mathcal{F} = -k_B \sum_s P_s \log P_s \quad (4.7)$$

Here,  $P_s = \mathcal{P}(E_s) = 1/g_s$ , and this function is called a “fairness” function [22]. By “fairness” it is meant that  $\mathcal{F}$  is a function of probabilities,  $\mathcal{F}(P_1, P_2, P_3, \dots, P_n)$ , and thus measures bias in a probability distribution. The least-bias approach then uses the method of Lagrange multipliers to maximize this fairness function, which is essentially obtaining the entropy of the system by selecting the “least-biased” set of unknown probabilities. “Equivalently, it is the basis of a statistical inversion procedure to infer least biased probabilities that are consistent with relevant thermodynamic measureables” [22]. This is a useful approach to the Seebeck problem, because the Seebeck coefficient is a function of a thermodynamic quantity, the chemical potential.

#### 4.2.1 Forming the Lagrangian

The system is also considered to be an “open system,” one in which particle number changes. For our purposes, “particles” are just the carriers. Thus, the grand canonical or thermodynamic Hamiltonian,  $\hat{\mathcal{H}}$ , given by

$$\hat{\mathcal{H}} = \mathcal{H}_{op} - \mu \mathcal{N}_{op}, \quad (4.8)$$

is used to describe the system. The thermodynamic Hamiltonian is composed of the canonical Hamiltonian,  $\mathcal{H}_{op}$ , which for our purposes will contain the Hubbard Hamiltonian. The second piece of the thermodynamic Hamiltonian is the particle number operator,  $\mathcal{N}_{op}$ , and the chemical potential,  $\mu$ . It is precisely expression (4.8) that gives the chemical potential meaning as an energy per particle [23]. Here, both  $\mathcal{H}_{op}$  and  $\mathcal{N}_{op}$  are operators with their own eigenvalue equations. Taking  $|\varphi_s\rangle$  to be the eigenstate corresponding to state  $s$  that is a simultaneous eigenstate of  $\hat{\mathcal{H}}$ ,  $\mathcal{H}_{op}$

and  $\mathcal{N}_{op}$ , yields the eigenvalue equation for  $\hat{\mathcal{H}}$ ,

$$\hat{\mathcal{H}}|\varphi_s\rangle = (\langle\mathcal{H}_{op}\rangle - \mu\langle\mathcal{N}_{op}\rangle)|\varphi_s\rangle. \quad (4.9)$$

The eigenvalues for  $\mathcal{H}_{op}$  and  $\mathcal{N}_{op}$ ,  $\varepsilon_s$  and  $N$  respectively, will further be defined as

$$\begin{aligned} \mathcal{H}_{op}|\varphi_s\rangle &= E_s|\varphi_s\rangle \\ \mathcal{N}_{op}|\varphi_s\rangle &= N|\varphi_s\rangle \end{aligned} \quad (4.10)$$

Recall from statistical mechanics that if we let  $\mathcal{P}[\varepsilon_s(N)]$  be the probability that the system is in state  $s$  with energy  $\varepsilon_s$  and  $N$  number of carriers, the expectation value for  $\hat{\mathcal{H}}$  can be written as

$$\langle\hat{\mathcal{H}}\rangle = \langle\mathcal{H}_{op}\rangle - \mu\langle\mathcal{N}_{op}\rangle \quad (4.11)$$

$$\langle\hat{\mathcal{H}}\rangle = \sum_{N=0,1,2,\dots}^S \varepsilon_s(N) \mathcal{P}[E_s(N)] - \mu \sum_{N=0,1,2,\dots}^S N \mathcal{P}[E_s(N)]. \quad (4.12)$$

The expectation value for  $\hat{\mathcal{H}}$  will be needed as a constraint in the Lagrangian equation, described in Appendix D.

In the case of the Seebeck problem,  $\langle\mathcal{H}_{op}\rangle$  is given by

$$\langle\mathcal{H}_{op}\rangle = E_{system} + \langle H_{Hubbard} \rangle. \quad (4.13)$$

Since the cases we are interested in calculating for comparison with Chaikin and Beni's work fall in the regime of a small transfer matrix element, namely  $k_B T \gg t$ , we are only interested in the limit  $t \rightarrow 0$ . Taking this limit in the Hubbard Hamiltonian given by (3.6), the average value,  $\langle\mathcal{H}_{op}\rangle$ , becomes

$$\begin{aligned} \langle \mathcal{H}_{op} \rangle = E_{system} + \sum_{n_1, n_2, \dots, n_N} \left[ U_o \sum_{i, \sigma} n_{i, \sigma} n_{i, -\sigma} \right. \\ \left. + \sum_{i, j, \sigma, \sigma'} U_{j, \sigma} n_{i, \sigma} n_{i+j, \sigma'} \right] \mathcal{P}[\varepsilon_s(n_1, n_2, \dots, n_N)] \end{aligned} \quad (4.14)$$

Note that the energy of the system,  $E_{system}$ , arises from the “on-site” energy terms  $\sim t_o C_i^\dagger C_i$ , which are not involved in the “hopping.” Assume that each particle has the same energy,  $\varepsilon$ . In the case of the Seebeck problem, we can think of this as a binding energy for the carrier to bind to an atomic site. Thus, taking spin into account,  $E_{system}$  can be written as

$$E_{system} = \sum_{n_1, n_2, \dots, n_N} \left[ \sum_{i, \sigma} (n_{i, \sigma} + n_{i, -\sigma}) \varepsilon \right] \mathcal{P}[\varepsilon_s(n_1, n_2, \dots, n_N)]. \quad (4.15)$$

Furthermore, since the particles are assumed to have the same energy, the probabilities associated with each state are now equivalent. Thus  $\mathcal{P}[\varepsilon_s(n_1, n_2, \dots, n_N)]$  can be replaced by  $\mathcal{P}(n_1, n_2, \dots, n_N)$ . Using this with (4.10),  $\langle \mathcal{H}_{op} \rangle$  can be rewritten as

$$\begin{aligned} \langle \mathcal{H}_{op} \rangle = \sum_{n_1, n_2, \dots, n_N} \left[ \sum_{i, \sigma} (n_{i, \sigma} + n_{i, -\sigma}) \varepsilon + U_o \sum_{i, \sigma} n_{i, \sigma} n_{i, -\sigma} \right. \\ \left. + \sum_{i, j, \sigma, \sigma'} U_{j, \sigma} n_{i, \sigma} n_{i+j, \sigma'} \right] \mathcal{P}(n_1, n_2, \dots, n_N) \end{aligned} \quad (4.16)$$

Substituting (4.13) for the average value  $\langle \mathcal{H}_{op} \rangle$  in equation (4.8), the Lagrangian determined in Appendix D can be written as

$$\begin{aligned}
\mathcal{L} = & -k_B \sum_{n_1, n_2, \dots, n_N} \mathcal{P}(n_1, n_2, \dots, n_N) \log \mathcal{P}(n_1, n_2, \dots, n_N) \\
& -\lambda_o \sum_{n_1, n_2, \dots, n_N} \mathcal{P}(n_1, n_2, \dots, n_N) \\
& -\lambda_1 \left\{ \sum_{n_1, n_2, \dots, n_N} \left[ \sum_{i, \sigma} (n_{i, \sigma} + n_{i, -\sigma}) \varepsilon + U_o \sum_{i, \sigma} n_{i, \sigma} n_{i, -\sigma} \right. \right. \\
& \quad \left. \left. + \sum_{i, j, \sigma, \sigma'} U_{j, \sigma} n_{i, \sigma} n_{i+j, \sigma'} \right] \mathcal{P}(n_1, n_2, \dots, n_N) \right. \\
& \quad \left. - \mu \sum_{N=n_1, n_2, \dots, n_N} (n_{i, \sigma} + n_{i, -\sigma}) \mathcal{P}(n_1, n_2, \dots, n_N) \right\}
\end{aligned} \tag{4.17}$$

#### 4.2.2 Maximizing the Lagrangian

The next step in the method of Lagrange multipliers is to maximize the function. This is done using the usual method for finding an extremum, namely by taking the partial derivative of the Lagrangian with respect to the probability that the system is in some state  $k$ , given by  $P_k \equiv \mathcal{P}(n_1, n_2, \dots, n_N)$ , and setting the derivative equal to zero. Note that doing so will result in selecting only the  $P_k$  terms from the sums, since all other terms will be zero. This result is given by

$$\begin{aligned}
0 = \frac{\partial \mathcal{L}}{\partial P_k} = & -k_B (1 + \log P_k) - \lambda_o \\
& -\lambda_1 \left[ \sum_{i, \sigma} (n_{i, \sigma} + n_{i, -\sigma}) \varepsilon + U_o \sum_{i, \sigma} n_{i, \sigma} n_{i, -\sigma} \right. \\
& \quad \left. + \sum_{i, j, \sigma, \sigma'} U_{j, \sigma} n_{i, \sigma} n_{i+j, \sigma'} - \mu \sum_{i, \sigma} (n_{i, \sigma} + n_{i, -\sigma}) \right]
\end{aligned} \tag{4.18}$$

Since constants will contribute zero during this derivative step, one may choose to not include the constant value to which the constraint is set.

Using (4.18), the equation for  $P_k$  can be determined,

$$P_k = e^{-\frac{\lambda_0}{k_B}} e^{-\frac{\lambda_1}{k_B} \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}. \quad (4.19)$$

Following the method of Lagrange multipliers, applying the first constraint yields

$$\sum_k P_k = \sum_{n_1, n_2, \dots, n_N} \mathcal{P}(n_1, n_2, \dots, n_N) = 1, \quad (4.20)$$

which is that the sum of the probabilities must equal one. Solving (4.20) by substituting the expression for  $P_k$  given by (4.19), yields an expression for the Lagrange multiplier,  $\lambda_0$ ,

$$e^{-\frac{\lambda_0}{k_B}} = \frac{e}{\sum_{n_1, n_2, \dots, n_N} e^{-\frac{\lambda_1}{k_B} \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}}. \quad (4.21)$$

Substituting (4.21) into (4.19) yields an equation for the probability, given here by

$$P_k = \frac{e^{-\frac{\lambda_1}{k_B} \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}}{\sum_{n_1, n_2, \dots, n_N} e^{-\frac{\lambda_1}{k_B} \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}}. \quad (4.22)$$

Note that by doing so, the Lagrange multiplier  $\lambda_0$  has been eliminated.

### 4.2.3 The Grand Partition Function

Once the probability function has been determined, the next step is to find the grand partition function for the system. Note that by definition, this is the normalizing denominator of the probability expression (4.21). Thus, the grand partition function,  $\mathcal{Z}_{gr}$ , is given by

$$\mathcal{Z}_{gr} = \sum_{n_1, n_2, \dots, n_N} e^{-\frac{\lambda_1}{k_B} \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}. \quad (4.23)$$

Consistency with thermodynamics, i.e. the First Law, requires  $\frac{\lambda_1}{k_B} = \frac{1}{k_B T}$ . Thus let  $\beta = 1/k_B T$  replace the Lagrange multiplier term present in (4.23). Doing so yields the final form for the grand partition function,

$$\mathfrak{Z}_{gr} = \sum_{n_1, n_2, \dots, n_N} e^{-\beta \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + \sum_{i,j,\sigma,\sigma'} U_{j,\sigma} n_{i,\sigma} n_{i+j,\sigma'} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}, \quad (4.24)$$

that will be used to calculate the chemical potential, and ultimately the Seebeck coefficient.

### 4.3 Application to Seebeck coefficient problem

The Seebeck coefficient can then be calculated using the partition function given by (4.24). Recall from the discussion in Chapter 3 that the Seebeck coefficient in the high temperature regime is given by

$$S(T \rightarrow \infty) = -\frac{\mu}{qT}. \quad (4.25)$$

The approach for determining the Seebeck coefficient is as follows. In statistical mechanics, the average number of particles,  $\langle N \rangle$ , is by definition a function of the grand partition function,

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log \mathfrak{Z}_{gr}. \quad (4.26)$$

Note that since none of the cases to be compared with Chaikin and Beni's work include nearest-neighbor interaction terms, the limit  $U_j \rightarrow 0$  is taken immediately, reducing the grand partition function to

$$\mathfrak{Z}_{gr} = \sum_{n_1, n_2, \dots, n_N} e^{-\beta \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}. \quad (4.27)$$

Then,  $\langle N \rangle / N$  will be replaced by  $\rho$ , which represents average number of carriers on occupied sites per total number of sites, i.e. the carrier concentration. The remaining expression can be rearranged such that chemical potential,  $\mu$ , will be a function of  $\rho$ . Replacing  $\mu$  in (4.25) with the expression for  $\mu$  as a function of  $\rho$  will yield an expression for the Seebeck coefficient as a function of  $\rho$ . It is this expression of the Seebeck coefficient that will be compared with the results from the Chaikin and Beni paper, discussed in Chapter 3.

## 4.4 Calculations and Results

### 4.4.1 Heikes Formula

The Heikes case is characterized by a system of spinless fermions on atomic sites, where only single occupancy is allowed. Since spin is not considered, the grand partition function given by (4.27) reduces to

$$\mathcal{Z}_{gr} = \sum_{n_1, n_2, \dots, n_N} e^{-\beta \left[ \sum_{i,\sigma} (\epsilon - \mu) n_i \right]}. \quad (4.28)$$

Note that in this case, the onsite Coulomb interaction,  $U_o$ , goes to zero because this interaction cannot exist if only single occupancy is allowed. Expanding the sum in the exponent of (4.28) yields

$$\mathcal{Z}_{gr} = \sum_{n_1, n_2, \dots, n_N} e^{-\beta(\epsilon - \mu)n_1} e^{-\beta(\epsilon - \mu)n_2} \dots e^{-\beta(\epsilon - \mu)n_N}. \quad (4.29)$$

At this point, the assumption is made that all the carriers are identical. Thus, (4.29) can be simplified, and rewritten as

$$\mathcal{Z}_{gr} = \left[ \sum_n e^{-\beta(\epsilon - \mu)n} \right]^N. \quad (4.30)$$

Now consider the possible occupation numbers,  $n$ . In the Heikes case described

above, double occupancy is not allowed. Thus, possible occupations are zero or one carrier per site,  $n = 0, 1$ . Completing the sum in (4.30) with these occupations yields

$$\mathcal{Z}_{gr} = \left[ \sum_{n=0,1} e^{-\beta(\varepsilon-\mu)n} \right]^N = \left[ 1 + e^{-\beta(\varepsilon-\mu)} \right]^N. \quad (4.31)$$

Note that the grand partition function is now in a closed form. The binding energy can also be set to zero without loss of generality,

$$\mathcal{Z}_{gr} = \left( 1 + e^{\beta\mu} \right)^N. \quad (4.32)$$

Making the substitution,  $e^{\beta\mu} \rightarrow \lambda$ , in the grand partition function (4.32) together with (4.27) yields

$$\langle N \rangle = \frac{N\lambda}{1 + \lambda}. \quad (4.33)$$

The carrier concentration is then given by

$$\rho = \langle N \rangle / N = \frac{\lambda}{1 + \lambda}. \quad (4.34)$$

Solving for  $\lambda = \lambda(\rho)$  yields

$$\lambda = \frac{\rho}{1 - \rho}. \quad (4.35)$$

Replacing the substituted value,  $\lambda$ , with the original expression,  $e^{\beta\mu}$ , allows for solving of the chemical potential as a function of  $\rho$ ,

$$\mu = \frac{1}{\beta} \log \left( \frac{\rho}{1 - \rho} \right). \quad (4.36)$$

Finally, the Seebeck coefficient for this case can be calculated using (4.25) and the chemical potential given by (4.36),



$$S(T \rightarrow \infty) = \frac{k_B}{q} \log \left( \frac{1-\rho}{\rho} \right). \quad (4.37)$$

Note that if the charge carriers are chosen to be electrons,  $q \rightarrow -e$ , as is the case presented in the Chaikin and Beni paper, the Seebeck coefficient calculated using this least-bias method precisely matches that presented in the aforementioned paper, given by (3.8).

#### 4.4.2 General Solution, no nearest-neighbor interaction

A general solution for the Seebeck coefficient can be found for the case that allows double-occupancy and considers the spin of the carrier. Examining the limiting cases of this solution will yield results for comparison with those in Chaikin and Beni's paper, as discussed in Sections 3.2.1.2 and 3.2.1.3.

For this case, the grand partition function is given by (4.27). Again, a closed form of the grand partition function can be found by assuming the carriers are identical,

$$\mathcal{Z}_{gr} = \left[ 1 + 2e^{-\beta(\epsilon-\mu)} + e^{-2\beta(\epsilon-\mu)} e^{-\beta U_o} \right]^N. \quad (4.38)$$

Following the same steps of the least-bias approach, as discussed in the previous section for the Heikes case, the solution for the Seebeck coefficient is

$$S(T \rightarrow \infty) = \frac{k_B}{q} \log \left[ \frac{(\rho-2)e^{-\beta(\epsilon+U_o)}}{(1-\rho) \pm \sqrt{(\rho^2-2\rho)(1-e^{-\beta U_o})} + 1} \right]. \quad (4.39)$$

Note that the Seebeck coefficient given by (4.39) contains more information than was available using the approach of Chaikin and Beni. Recall that each of their results was a function only of carrier concentration. Here, (4.39) still contains a temperature dependence, hidden in the  $\beta$  term. Additionally, (4.39) is a function of the on-site Coulomb interaction,  $U_o$ , allowing one to examine the effects of a finite Coulomb interaction.

#### 4.4.2.1 Interacting Systems, fermions with spin

A limiting case of (4.39) is examined for comparison with Chaikin and Beni's results. This case considers there to be no on-site Coulomb interaction between the carriers, thus single occupancy and double occupancy are equally probable. The following limit is taken,  $U_o \rightarrow 0$ , and the Seebeck coefficient becomes

$$S(T \rightarrow \infty, U_o \rightarrow 0) = \frac{k_B}{q} \log \left[ \frac{(\rho - 2)e^{-\beta\epsilon}}{(1 - \rho) \pm 1} \right]. \quad (4.40)$$

Note that choosing the positive case in the denominator yields a negative argument in the logarithmic term for all positive binding energies, and causes the Seebeck coefficient to be always imaginary. Since the Seebeck coefficient is by definition an observable, and thus cannot be imaginary, only the negative case will be further examined,

$$S(T \rightarrow \infty, U_o \rightarrow 0) = \frac{k_B}{q} \log \left[ \frac{(2 - \rho)e^{-\beta\epsilon}}{\rho} \right]. \quad (4.41)$$

Note that if the charge of the carrier is replaced by that of an electron, and the binding energy,  $\epsilon$ , is taken to be zero, (4.41) precisely matches the corresponding result in the Chaikin and Beni paper, given by (3.9).

#### 4.4.2.2 Interacting Systems, on-site repulsion

Another limiting case of (4.39) is examined for comparison with Chaikin and Beni's results. This case considers there to be a strong on-site Coulomb interaction between the carriers, such that only single occupancy is allowed. Thus the following limit is taken,  $U_o \rightarrow \infty$ , and the Seebeck coefficient is given by

$$S(T \rightarrow \infty, U_o \rightarrow \infty) = \frac{k_B}{q} \log \left[ \frac{0}{(1 - \rho) \pm (\rho - 1)} \right]. \quad (4.42)$$

Choice of the negative sign yields a zero argument in the logarithmic term, causing the

limit of Seebeck coefficient to go to negative infinity. However, choosing the positive case yields a 0/0 argument in the logarithmic term. Since we are examining a limiting case, we can use l'Hôpital's rule,

$$\lim \left[ \frac{f(x)}{g(x)} \right] = \lim \left[ \frac{f'(x)}{g'(x)} \right]. \quad (4.43)$$

Let the original logarithm term in (4.39) be defined as  $f(U_o)/g(U_o)$ ,

$$\frac{f(U_o)}{g(U_o)} = \frac{(\rho - 2)e^{-\beta(\varepsilon + U_o)}}{(1 - \rho) + \sqrt{(\rho^2 - 2\rho)(1 - e^{-\beta U_o})} + 1} \quad (4.44)$$

Taking derivatives of the numerator and denominator with respect to  $U_o$  yields  $f'(U_o)$  and  $g'(U_o)$ ,

$$f'(U_o) = \beta(2 - \rho)e^{-\beta(\varepsilon + U_o)} \quad (4.45)$$

$$g'(U_o) = \frac{\beta(\rho^2 - 2\rho)e^{-\beta U_o}}{2\sqrt{(\rho^2 - 2\rho)(1 - e^{-\beta U_o})} + 1} \quad (4.46)$$

Using (4.45) and (4.47),  $f'(U_o)/g'(U_o)$  is constructed,

$$\frac{f'(U_o)}{g'(U_o)} = \frac{-2e^{-\beta\varepsilon} \sqrt{(\rho^2 - 2\rho)(1 - e^{-\beta U_o})} + 1}{\rho}. \quad (4.47)$$

Applying l'Hôpital's rule, examine the limit  $U_o \rightarrow \infty$ ,

$$\lim_{U_o \rightarrow \infty} \frac{f(U_o)}{g(U_o)} = \lim_{U_o \rightarrow \infty} \frac{f'(U_o)}{g'(U_o)} = \frac{2e^{-\beta\varepsilon}(1 - \rho)}{\rho}. \quad (4.48)$$

Thus the Seebeck coefficient for an infinite on-site Coulomb interaction, causing only single occupancy to be allowed, is given by

$$S(T \rightarrow \infty, U_o \rightarrow \infty) = \frac{k_B}{q} \log \left[ \frac{2e^{-\beta\epsilon}(1-\rho)}{\rho} \right]. \quad (4.49)$$

If the charge carriers are chosen to be electrons, and the binding energy,  $\epsilon$ , is taken to be zero, (4.49) precisely matches the corresponding result in the Chaikin and Beni paper, given by (3.10).

#### 4.5 Discussion of Results

The least-bias approach examined in this chapter is used to determine the Seebeck coefficient in the high-temperature limit for narrow-band materials with carriers whose transport mechanism is hopping, and whose interactions are described by the terms in the Hubbard Hamiltonian. This approach utilizes the thermodynamic understanding of the chemical potential and its relationship to the Seebeck coefficient. Incorporating the chemical potential gives the parameters physical meaning, and yields a temperature-dependent equation for the Seebeck coefficient, as a function of a carrier concentration parameter. Limiting cases of this Seebeck coefficient solution compare well with the results presented in the Chaikin and Beni paper discussed in the literature review in Chapter 3.

Additionally, the least-bias approach is not limited to one-dimension, as is often the case for the Chaikin and Beni results. Their approach for calculating the degeneracy parameter, upon which their chemical potential is based, can be restricted by the dimension of the configurations. They note in the conclusion of their publication that problems which involve only on-site interactions, such as equations (3.9) and (3.10), are valid for any number of dimensions [15]. Thus, it makes sense that these compare exactly with the limiting cases of the results from the least-bias approach.

Furthermore, the reason the least-bias results and the Chaikin and Beni cases (examined in Chapter 3) compare well is not coincidence, but rather due to a subtle feature shared by both approaches. Both approaches treat the Seebeck coefficient as an entropy problem. Chaikin and Beni use Boltzmann's entropy to *define* the chemical

potential, and calculate it indirectly by means of a degeneracy parameter. Although the least-biased approach allows one to calculate the chemical potential directly, the underlying assumption of the least-biased approach is that the case of least-bias (i.e. the most probable case) is being examined, since the method of Lagrange multipliers is applied to maximize the uncertainty function for the system.

## 5 HUBBARD CHAIN

### 5.1 Introduction

The purpose of the one-dimensional Hubbard chain is essentially the same as that of the one-dimensional Ising chain, to examine a chain of interacting atoms. Important features of the Ising model are discussed briefly in Appendix E. The interactions between atoms in the Hubbard chain are precisely those determined by the Hubbard Hamiltonian. The Hubbard chain is useful for the same reasons as the Ising chain, namely that it produces a closed form solution of the grand partition function. Additionally, the same grand partition function can also be found by using the transfer matrix approach of the Ising chain. This approach utilizes a matrix that contains all the possible interatomic interactions, and its eigenvalues can be used to form the grand partition function. This approach will be described in more detail in the following section.

### 5.2 Transfer Matrix Approach

In this section, the transfer matrix approach is applied to the Hubbard chain and to the Seebeck problem. First, consider the following Hubbard chain interactions as described in Chapter 3: on-site binding energy, on-site Coulomb interactions, and near-neighbor Coulomb interactions. In addition to these interactions, each atomic site also has a given number of possible occupations for carriers of a given spin.

For our purposes, the problem is simplified to consider only the on-site binding energy, the on-site Coulomb interaction and the  $j = i + 1$  nearest-neighbor interaction. Additionally, zero, one or two spin-1/2 carriers may occupy an atomic site. Thus, the total Hamiltonian is as follows,

$$H = \hat{H}_{Hubbard} - \mu \hat{N} \quad (5.1)$$

$$\begin{aligned}
H = & \epsilon \sum_i (n_{i,\uparrow} + n_{i,\downarrow}) + U_o \sum_i n_{i,\uparrow} n_{i,\downarrow} \\
& + U_1 \sum_i (n_{i,\uparrow} n_{j,\uparrow} + n_{i,\uparrow} n_{j,\downarrow} + n_{i,\downarrow} n_{j,\uparrow} + n_{i,\downarrow} n_{j,\downarrow}) - \mu \sum_i (n_{i,\uparrow} + n_{i,\downarrow}).
\end{aligned} \quad (5.2)$$

Here,  $n_i$  represents the occupation on the  $i^{th}$  atomic site. The arrow subscript denotes the spin of the carrier. Each element in the transfer matrix corresponds to a possible occupation. For example, one element corresponds to zero occupation on both the  $i^{th}$  and  $j^{th}$  sites. Another corresponds to one spin up carrier on the  $i^{th}$  site and zero occupation on the  $j^{th}$  site, etc. Thus, define the function that describes the occupation for that site as follows,

$$P(i_\uparrow, i_\downarrow, j_\uparrow, j_\downarrow) = e^{-\beta[(\epsilon - \mu)(i_\uparrow + i_\downarrow) + U_o(i_\uparrow i_\downarrow) + U_1(i_\uparrow j_\uparrow + i_\uparrow j_\downarrow + i_\downarrow j_\uparrow + i_\downarrow j_\downarrow)]} \quad (5.3)$$

Since up to two carriers are allowed per site, and per nearest-neighbor site, (5.3) must be a function of four variables, as shown. Each variable represents a carrier that is either present or not present; this is represented by replacing the variable with one or zero, respectively. Thus there are  $2^4 = 16$  possible occupation scenarios, and the transfer matrix will be a  $4 \times 4$  matrix is as follows,

$$\mathbf{P} = \begin{pmatrix} P(0,0,0,0) & P(0,0,1,0) & P(0,0,0,1) & P(0,0,1,1) \\ P(0,1,0,0) & P(0,1,1,0) & P(0,1,0,1) & P(0,1,1,1) \\ P(1,0,0,0) & P(1,0,1,0) & P(1,0,0,1) & P(1,0,1,1) \\ P(1,1,0,0) & P(1,1,1,0) & P(1,1,0,1) & P(1,1,1,1) \end{pmatrix}. \quad (5.4)$$

Applying the zero and one substitutions into  $P(i_\uparrow, i_\downarrow, j_\uparrow, j_\downarrow)$  given by (5.3) yields

$$\mathbf{P} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ e^{-\beta(\epsilon - \mu)} & e^{-\beta(U_1 + \epsilon - \mu)} & e^{-\beta(U_1 + \epsilon - \mu)} & e^{-\beta(2U_1 + \epsilon - \mu)} \\ e^{-\beta(\epsilon - \mu)} & e^{-\beta(U_1 + \epsilon - \mu)} & e^{-\beta(U_1 + \epsilon - \mu)} & e^{-\beta(2U_1 + \epsilon - \mu)} \\ e^{-\beta[U_o + 2(\epsilon - \mu)]} & e^{-\beta[2U_1 + U_o + 2(\epsilon - \mu)]} & e^{-\beta[2U_1 + U_o + 2(\epsilon - \mu)]} & e^{-\beta[4U_1 + U_o + 2(\epsilon - \mu)]} \end{pmatrix}. \quad (5.5)$$

The next step in the transfer matrix approach a chain of  $N$  atoms is to determine the

eigenvalues of the transfer matrix. These eigenvalues for a  $M \times M$  matrix are then summed as follows to determine the grand partition function,

$$\mathcal{Z}_{gr} = \lambda_1^N + \lambda_2^N + \cdots + \lambda_M^N \quad (5.6)$$

Once the grand partition function is determined, the same steps are followed to determine the Seebeck coefficient as outlined in Section 4.3.

### 5.3 Calculations and Results

#### 5.3.1 Excluding Nearest Neighbors

First the case of no nearest-neighbors is considered. Thus the limiting case of  $U_1 \rightarrow 0$  is taken for the transfer matrix given by (5.5), which yields

$$\mathbf{P} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ e^{-\beta(\varepsilon-\mu)} & e^{-\beta(\varepsilon-\mu)} & e^{-\beta(\varepsilon-\mu)} & e^{-\beta(\varepsilon-\mu)} \\ e^{-\beta(\varepsilon-\mu)} & e^{-\beta(\varepsilon-\mu)} & e^{-\beta(\varepsilon-\mu)} & e^{-\beta(\varepsilon-\mu)} \\ e^{-\beta[U_o+2(\varepsilon-\mu)]} & e^{-\beta[U_o+2(\varepsilon-\mu)]} & e^{-\beta[U_o+2(\varepsilon-\mu)]} & e^{-\beta[U_o+2(\varepsilon-\mu)]} \end{pmatrix} \quad (5.7)$$

There are four eigenvalues for this case,

$$\lambda_1 = \lambda_2 = \lambda_3 = 0 \quad (5.8)$$

$$\lambda_4 = 1 + 2e^{-\beta(\varepsilon-\mu)} + e^{-\beta U_o} e^{-2\beta(\varepsilon-\mu)}. \quad (5.9)$$

Using (5.6) to solve for the grand partition function yields

$$\mathcal{Z}_{gr} = \left[ 1 + 2e^{-\beta(\varepsilon-\mu)} + e^{-\beta U_o} e^{-2\beta(\varepsilon-\mu)} \right]^N. \quad (5.10)$$

Following the same procedure as outlined in Section 4.3, the Seebeck coefficient is

$$S(T \rightarrow \infty) = \frac{k_B}{q} \log \left[ \frac{(\rho - 2)e^{-\beta(\varepsilon+U_o)}}{(1 - \rho) \pm \sqrt{(\rho^2 - 2\rho)(1 - e^{-\beta U_o})} + 1} \right]. \quad (5.11)$$

Note that (5.11) precisely matches the result from the least-bias approach, (4.39). Thus



the limiting cases examined in Sections 4.4.2.1 and 4.4.2.2, and their comparison to the Chaikin and Beni results, are equally valid here.

Thus, the transfer matrix provides an alternate approach for calculating the grand partition function, yet follows the same steps of the least-bias approach to complete the calculation of the Seebeck coefficient.

### 5.3.2 *The Nearest-Neighbor Problem*

A solution to the nearest-neighbor problem is found by calculating the four eigenvalues of the transfer matrix given by (5.5). These eigenvalues were calculated using Mathematica, and the results were too lengthy for a grand partition function of the form (5.6) to be formed. Thus a Seebeck coefficient, in principle obtainable, could not conveniently be calculated for this case using the transfer matrix method.

## 5.4 **Discussion of Results**

Although both the least-bias method and Hubbard chain approach yield the same result, there are subtle differences that surround the two approaches. Although the least-bias approach may be easier to follow since thermodynamic quantities are methodically calculated, the transfer matrix bypasses all of these calculations, and simply uses its eigenvalues to determine the end result of a grand partition function. It should also be noted that the closed form for the grand partition function using the least-bias approach directly results from the fact that the summation in (4.27) could easily be represented in a closed form. Had the nearest neighbor interaction,  $U_1$ , been included in this summation, the closed form of the solution is no longer obvious and we cannot complete the least-bias approach. In this respect, the transfer matrix approach ensures a closed-form solution for the one-dimensional chain because of its origin in the Ising model and the nature of a linear algebra problem. Thus, the transfer matrix approach is not limited by one's ability to recognize the closed form of a summation, but rather by the ability to take complicated eigenvalues to the  $N^{\text{th}}$  power.

The resulting partition function should be the same for both approaches since both methods contain the same physical information; the transfer matrix just allows for an alternate way of doing the calculation. Additionally, since the partition function is the starting point for determining the Seebeck coefficient it makes sense that (5.11) is equivalent to (4.39), and that the limiting cases still agree with the Chaikin and Beni results in Section 3.2.

## 6 APPLICATION: TWO-ATOM SYSTEM

### 6.1 Introduction

In the final process of fabricating p-type thin film transparent conductive oxide (TCO)  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ , the material is exposed to oxygen under pressure. This step intercalates oxygen into the lattice structure (see Section 6.2), which has the effect of introducing acceptor-like impurities (holes). These holes are assumed to thermally migrate from the intercalated oxygen to nearby copper sites providing the system with transport carriers under the influence of electric fields and/or temperature gradients. In particular, the measured Seebeck coefficient is examined by a thermodynamic theory constructed to determine carrier and material properties in the oxygen-doped thin film TCO compound  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ .

### 6.2 Oxygen Intercalation, $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$

The p-type TCO  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  is magnesium-doped copper scandium oxide, into which oxygen is intercalated at various pressures. The amount of oxygen in the material depends on the pressure at which the sample was intercalated, as is obvious even by visual inspection.

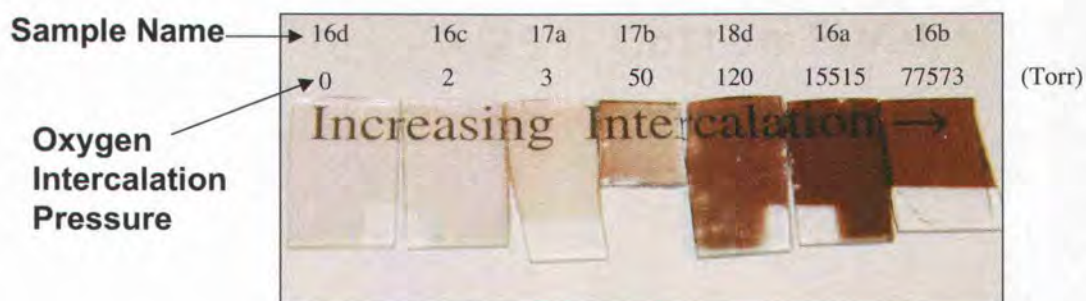


Figure 6.1  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  thin films intercalated at various oxygen pressures

This material has a delafossite crystal structure as shown in Figure 6.2.

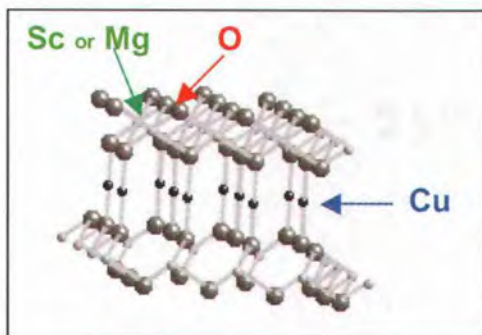


Figure 6.2 Delafossite Structure

Oxygen atoms surround a scandium or magnesium atom, while the copper atoms are located in a layer. The intercalation process represents a case of diffusive equilibrium in that the number of carriers on copper and oxygen sites will change with temperature while preserving a conservation of total carriers.

Each intercalated oxygen atom,  $O$ , enters the crystal structure with six electrons, and therefore two holes. The copper atoms in the delafossite structure are  $Cu^{I+}$ . The copper layer can accommodate the size of the oxygen atoms, so the intercalated oxygen atoms bond with copper atoms in this layer with one hole donated to each of two neighboring copper atoms, as illustrated in the cartoon below,

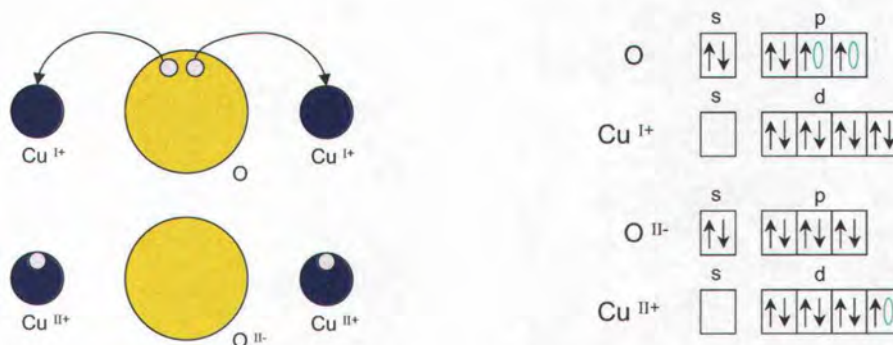


Figure 6.3 Introduction of carriers (holes)

Thus, with the loss of two holes, the oxygen atom becomes  $O^{II-}$  and thus has a filled  $s$  and  $p$  shell. Additionally,  $Cu^{I+}$  begins with a full  $d$  shell and becomes  $Cu^{II+}$  with the

addition of one hole. Furthermore, it is suggested by the fit of the theoretical model to the experimental results (Section 6.4) that the carriers originating on the intercalated oxygen atoms will either both go to copper sites or both remain on the oxygen atom, i.e. it is unlikely that only one carrier will go to a neighboring copper atom.

This process is, of course, equivalently and conveniently described in terms of electrons rather than holes. For example, after the intercalated  $O$  atom enters the copper layer, two neighboring  $Cu^{I+}$  atoms each donate one electron to the  $O$  atom. Thus  $O$  becomes  $O^{II-}$  since the atom gained two electrons. Each  $Cu^{I+}$  atom becomes  $Cu^{II+}$ , since they have each given away one electron. This viewpoint makes more evident the role of electron correlations on the oxygen sites.

In terms of electron occupation, the problem is described as follows. Each  $O$  and  $Cu^{I+}$  atom is an atomic site whose electron occupation can be described by the spin vector  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix}$ . The allowed electron occupations for the oxygen and copper sites are  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 1 \\ 1 \end{pmatrix}$  and  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \end{pmatrix}$  respectively. These occupations are described further in the following paragraphs.

Prior to electron thermalization, the intercalated  $O$  site has the electron occupation  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$  while each  $Cu^{I+}$  site has the electron occupation  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$  or  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ . If *both* neighboring  $Cu^{I+}$  atoms give an electron to the  $O$  atom, the  $O$  atom becomes  $O^{II-}$  and the electron occupation of its site is now  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ . With the loss of an electron, each  $Cu^{I+}$  atom is now  $Cu^{II+}$ , and the electron occupation of *its* site is now  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$ .

The intercalation result can be represented by a state of diffusive equilibrium, according to the following electron conservation equation,

$$\langle N_o \rangle + \langle N_{Cu} \rangle = N_{Cu}. \quad (6.1)$$

Thus, the sum of the average number of electrons on oxygen sites,  $\langle N_o \rangle$ , and copper sites,  $\langle N_{Cu} \rangle$ , must equal the total number of “available” electrons. Since each copper atom can contribute one electron to this process, the total number of “available” electrons is then just the total number of copper atoms,  $N_{Cu}$ . [In principle, the correlation energy between oxygen atoms and nearest neighbor copper atoms should play a role. But to a zeroth approximation this detail is neglected.]

### 6.3 Quantitative Procedure

The grand partition functions for electrons on copper and oxygen atoms can be determined using either the transfer matrix approach [see Section 5.2] or the least-biased approach [see Section 4.2]. Recall the general partition function determined in Section 4.2.3 for the Hubbard Hamiltonian case of no nearest neighbor interactions given by (4.27), repeated here,

$$\mathcal{Z}_{gr} = \sum_{n_1, n_2, \dots, n_N} e^{-\beta \left[ \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \epsilon + U_o \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} - \mu \sum_{i,\sigma} (n_{i,\sigma} + n_{i,-\sigma}) \right]}. \quad (6.2)$$

Applying the appropriate electron occupations for  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  yields the closed form of the grand partition function. As described in Section 6.2, the possible electron

occupations of the copper site are  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  or  $\begin{pmatrix} 0 \\ 0 \end{pmatrix}$ . Additionally, it is believed

that the possible electron occupations of the oxygen site are  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$  or  $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ .

However, we can verify this assumption by also examining the occupation of just one

electron on the oxygen site,  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$  or  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ , and comparing numeric results for the

Seebeck coefficient with that from experimental data on  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  samples. If

the best fit occurs when the oxygen on-site Coulomb interaction parameter is largely negative, this suggests that double-occupancy is highly favored.

Thus, there are two cases to consider. Case A examines all possible electron occupations on the oxygen site,  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  and  $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ . Comparison with experimental Seebeck data is used to determine the sign and magnitude of  $U_o$ . Case B considers a modified partition function of Case A, where the case of single occupancy is eliminated.

### 6.3.1 Case A

Applying the electron occupations for Case A yields the following grand partition functions,

$$\mathcal{Z}_{grCu} = \left[ 1 + 2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})} \right]^{N_{Cu}} \quad (6.3)$$

$$\mathcal{Z}_{grO} = \left[ 1 + 2e^{-\beta(\epsilon_O - \mu_O)} + e^{-\beta U_o} e^{-2\beta(\epsilon_O - \mu_O)} \right]^{N_O}. \quad (6.4)$$

Here,  $\mu_{Cu}$  and  $\mu_O$  are the chemical potentials for electrons on copper atoms and oxygen atoms, respectively. Similarly,  $N_{Cu}$  and  $N_O$  are the number of copper atoms and oxygen atoms, respectively. The binding energies  $\epsilon_{Cu}$  and  $\epsilon_O$ , are the energies required for an electron to occupy a site on a copper atom and an oxygen atom, respectively. Additionally, since the oxygen atom can have double occupancy,  $\begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ , the on-site coulomb interaction,  $U_o$ , describes the interaction energy of a second electron joining an electron of opposite spin already on the oxygen site.

Using the least-biased approach described in Section 4.3, the average number of electrons on copper atoms and oxygen atoms can be found. These calculations yield

$$\langle N_{Cu} \rangle = N_{Cu} \frac{2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}}{1 + 2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}} \quad (6.5)$$

$$\langle N_o \rangle = N_o \frac{2e^{-\beta(\epsilon_o - \mu_o)} + 2e^{-\beta U_o} e^{-2\beta(\epsilon_o - \mu_o)}}{1 + 2e^{-\beta(\epsilon_o - \mu_o)} + e^{-\beta U_o} e^{-2\beta(\epsilon_o - \mu_o)}}. \quad (6.6)$$

Next substitute (6.5) and (6.6) into the conservation equation describing the diffusive equilibrium process occurring within the material, given by (6.1),

$$N_{Cu} \frac{2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}}{1 + 2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}} + 2N_o \frac{e^{-\beta(\epsilon_o - \mu_o)} + e^{-\beta U_o} e^{-2\beta(\epsilon_o - \mu_o)}}{1 + 2e^{-\beta(\epsilon_o - \mu_o)} + e^{-\beta U_o} e^{-2\beta(\epsilon_o - \mu_o)}} = N_{Cu}. \quad (6.7)$$

Additionally, the state of diffusive equilibrium, by definition, requires the chemical potentials of all carriers to be equivalent,

$$\mu_{Cu} = \mu_o \rightarrow \mu. \quad (6.8)$$

Thus, let  $\mu$  be the chemical potential for all electrons in diffusive equilibrium. Making this substitution into (6.7) yields

$$\frac{2e^{-\beta(\epsilon_{Cu} - \mu)}}{1 + 2e^{-\beta(\epsilon_{Cu} - \mu)}} + 2 \left( \frac{N_o}{N_{Cu}} \right) \frac{e^{-\beta(\epsilon_o - \mu_o)} + e^{-\beta U_o} e^{-2\beta(\epsilon_o - \mu_o)}}{1 + 2e^{-\beta(\epsilon_o - \mu_o)} + e^{-\beta U_o} e^{-2\beta(\epsilon_o - \mu_o)}} = 1. \quad (6.9)$$

Next determine the carrier concentration that is of interest. For the case of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  define the intercalated atom concentration parameter as follows,

$$\rho = \frac{N_o}{N_{Cu}}. \quad (6.10)$$

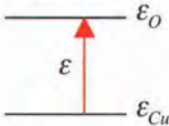
Here, the concentration,  $\rho$ , is the ratio of the number of oxygen atoms to copper atoms. This parameter will have more meaning as a concentration once the Langmuir model of surface adsorption is examined in the next section, where it becomes evident that this parameter gives an indication of the ratio of oxygen adsorbed by the copper “surface.”

Applying the change of variables given by (6.10) yields



$$\frac{2e^{-\beta(\epsilon_{Cu}-\mu)}}{1+2e^{-\beta(\epsilon_{Cu}-\mu)}} + 2\rho \frac{e^{-\beta(\epsilon_O-\mu_O)} + e^{-\beta U_o} e^{-2\beta(\epsilon_O-\mu_O)}}{1+2e^{-\beta(\epsilon_O-\mu_O)} + e^{-\beta U_o} e^{-2\beta(\epsilon_O-\mu_O)}} = 1. \quad (6.11)$$

To simplify (6.11), define the parameter  $\epsilon$  to be the difference of the copper binding energy and the oxygen binding energy,

$$\epsilon = \epsilon_O - \epsilon_{Cu}. \quad (6.12)$$


Thus the binding energies are defined as follows,

$$\begin{aligned} \epsilon_{Cu} &\rightarrow 0 \\ \epsilon_O &\rightarrow \epsilon \end{aligned} \quad (6.13)$$

At this point, continue with the least-biased approach and apply the following substitutions,

$$e^{\beta\mu} \rightarrow \lambda \quad (6.14)$$

$$e^{-\beta\epsilon} \rightarrow x \quad (6.15)$$

which yields,

$$\frac{2\lambda}{1+2\lambda} + 2\rho \frac{\lambda e^{-\beta\epsilon_O} + \lambda^2 x^2 e^{-\beta U_o}}{1+2\lambda e^{-\beta\epsilon_O} + \lambda^2 x^2 e^{-\beta U_o}} = 1. \quad (6.16)$$

At this point, solving for  $\lambda = \lambda(\rho)$  is a complicated calculation, but Mathematica makes it easy and a copy of this worksheet appears in Appendix F. Selecting an appropriate real root  $\lambda = \lambda(\rho)$ , the equation for the Seebeck coefficient, (4.25), can be rewritten in terms of  $\lambda$  instead of  $\mu$  since  $\mu = \frac{1}{\beta} \ln(\lambda)$ ,

$$S = -\frac{k_B}{q} \ln(\lambda). \quad (6.17)$$

Substituting the numeric value for Boltzmann's constant and the electron charge yields

a Seebeck coefficient that is a function of  $\rho$ ,  $\varepsilon$ ,  $U_o$  and  $T$ ,

$$S = 86.2 \ln(\lambda) \quad \mu\text{V}/\text{K}. \quad (6.18)$$

The Seebeck coefficient given by (6.18) is then examined as a function of temperature for various values of  $\rho$ ,  $\varepsilon$  and  $U_o$ .

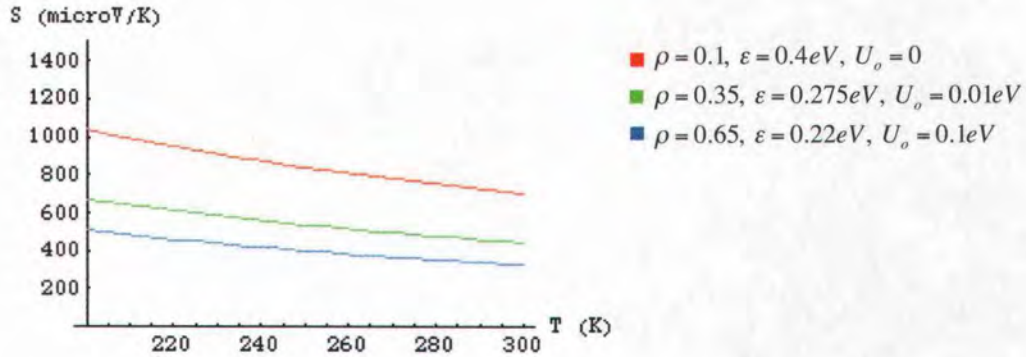


Figure 6.4 Example of Seebeck results

Figure 6.4 examines the Seebeck coefficient for positive values of the onsite oxygen Coulomb interaction,  $U_o$ , as well as for the case where  $U_o = 0$ .

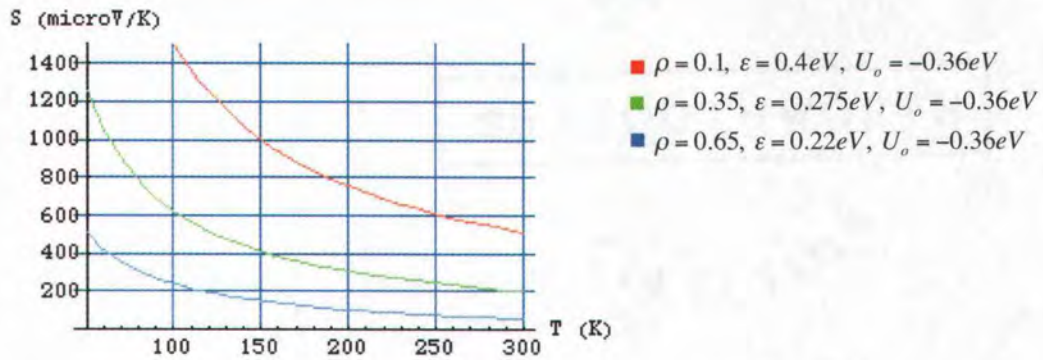


Figure 6.5 Example of Seebeck results

Figure 6.5 examines the Seebeck coefficient for the same values of  $\rho$  and  $\varepsilon$  as in Figure 6.4, now with negative values of the onsite Coulomb interaction,  $U_o$ .

Figures 6.4 and 6.5 strongly suggest that the on-site Coulomb parameter for oxygen



### 6.3.2 Case B

Case B considers the on-site Coulomb interaction for oxygen sites,  $U_o$ , to be large and negative, causing the double occupancy term in the oxygen grand partition function to dominate any single occupancy contribution. Applying the electron occupations for Case B yields the following grand partition functions,

$$\mathcal{Z}_{grCu} = \left[ 1 + 2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})} \right]^{N_{Cu}} \quad (6.19)$$

$$\mathcal{Z}_{grO} = \left[ 1 + e^{-2\beta(\epsilon_o - \mu_o)} \right]^{N_o}. \quad (6.20)$$

Variables are defined the same as in Case A. The average number of electrons on copper atoms and oxygen atoms is calculated using the least-biased approach,

$$\langle N_{Cu} \rangle = N_{Cu} \frac{2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}}{1 + 2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}} \quad (6.21)$$

$$\langle N_o \rangle = N_o \frac{2e^{-2\beta(\epsilon_o - \mu_o)}}{1 + e^{-2\beta(\epsilon_o - \mu_o)}}. \quad (6.22)$$

Substituting (6.21) and (6.22) into the conservation equation, (6.1), yields

$$N_{Cu} \frac{2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}}{1 + 2e^{-\beta(\epsilon_{Cu} - \mu_{Cu})}} + 2N_o \frac{e^{-2\beta(\epsilon_o - \mu_o)}}{1 + e^{-2\beta(\epsilon_o - \mu_o)}} = N_{Cu}. \quad (6.23)$$

Applying the same substitutions as in Case A, namely that of equivalent chemical potentials,  $\mu_{Cu} = \mu_o \rightarrow \mu$ , the definitions for the binding energies and concentration parameter, yields

$$\frac{2e^{-\beta\mu}}{1 + 2e^{-\beta\mu}} + 2\rho \frac{e^{-2\beta(\epsilon - \mu)}}{1 + e^{-2\beta(\epsilon - \mu)}} = 1. \quad (6.24)$$

Applying the substitutions,  $e^{\beta\mu} \rightarrow \lambda$  and  $e^{-\beta\epsilon} \rightarrow x$  yields

$$\frac{2\lambda}{1 + 2\lambda} + 2\rho \frac{\lambda^2 x^2}{1 + \lambda^2 x^2} = 1. \quad (6.25)$$



Solving for  $\lambda = \lambda(\rho)$  is examined in Mathematica and a copy of this worksheet appears in Appendix G. Assuming a solution  $\lambda = \lambda(\rho)$  is found, the equation for the Seebeck coefficient, (4.25), can be rewritten in terms of  $\lambda$  instead of  $\mu$ , according to (6.17). Substituting the numeric values for Boltzmann's constant and electron charge yields a Seebeck coefficient that is a function of  $\rho$ ,  $\varepsilon$  and  $T$ . A plot of this Seebeck coefficient as a function of temperature for various values of  $\rho$  and  $\varepsilon$  is examined in Figure 6.7.

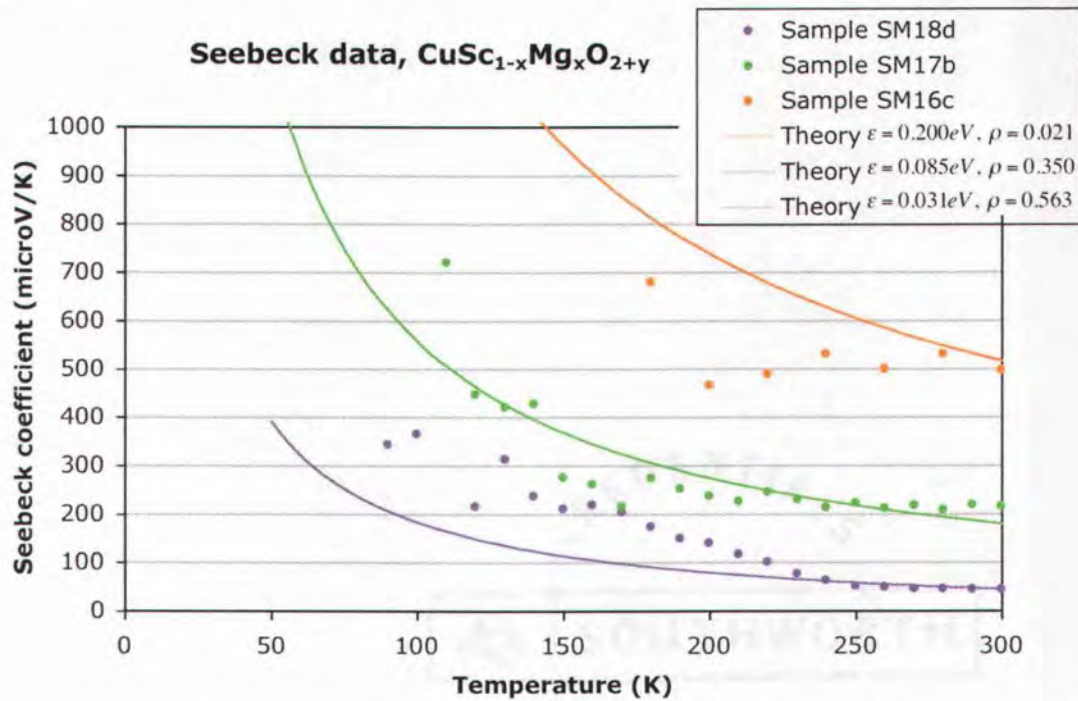


Figure 6.7 Comparison of experimental data for  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  samples and theoretical data

This comparison demonstrates that the theoretical representation of the physical material yields results in reasonable comparison to the experimental data. The oxygen binding energy,  $\varepsilon$ , decreases as the intercalated atom concentration,  $\rho$ , increases. The increase in  $\varepsilon$  is interpreted as the formation of an oxygen band. For example, the oxygen sites can be modeled as a periodic system, where each site is represented by a potential  $\varepsilon$ ,



Figure 6.8 Periodic system representation of oxygen atoms, with potentials  $\varepsilon$

As more oxygen atoms are introduced during intercalation, the intercalated atom concentration,  $\rho$ , increases, introducing overlap between potentials of neighboring sites and lifting the atomic degeneracy, i.e.  $\varepsilon \rightarrow \varepsilon \pm \Delta$ .

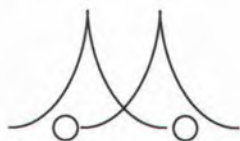


Figure 6.9 Overlapping potentials of neighboring oxygen atoms

The further addition of oxygen causes the oxygen band to continue to widen, perhaps even to the point of overlapping the copper band. The following cartoons describe the band picture of the situations examined in Figures 6.8 and 6.9.

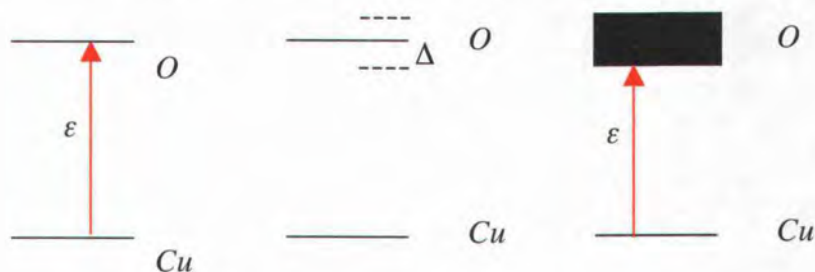


Figure 6.10 Cartoon of band picture

Figure 6.10 shows how the increase in  $\rho$  causes the oxygen band to widen, thus decreasing  $\varepsilon$ .

#### 6.4 Langmuir's Model of Surface Adsorption

The intercalation process examined in the previous section can be represented by Langmuir's surface model. The copper layer acts as a "surface" onto which the oxygen molecules are "adsorbed." Each of the physical samples shown in Figure 6.1 was intercalated in oxygen at various pressures, to introduce different amounts of carriers into the system. Experimental results demonstrated that the room temperature Seebeck coefficient of each sample was inversely related to the oxygen pressure at which it was intercalated. This suggests that the Seebeck coefficient should have an oxygen concentration dependence, and that this concentration is correlated to the intercalation pressure. A plot of the physical samples' Seebeck coefficients at room temperature and corresponding intercalation pressures is given in the following plot.

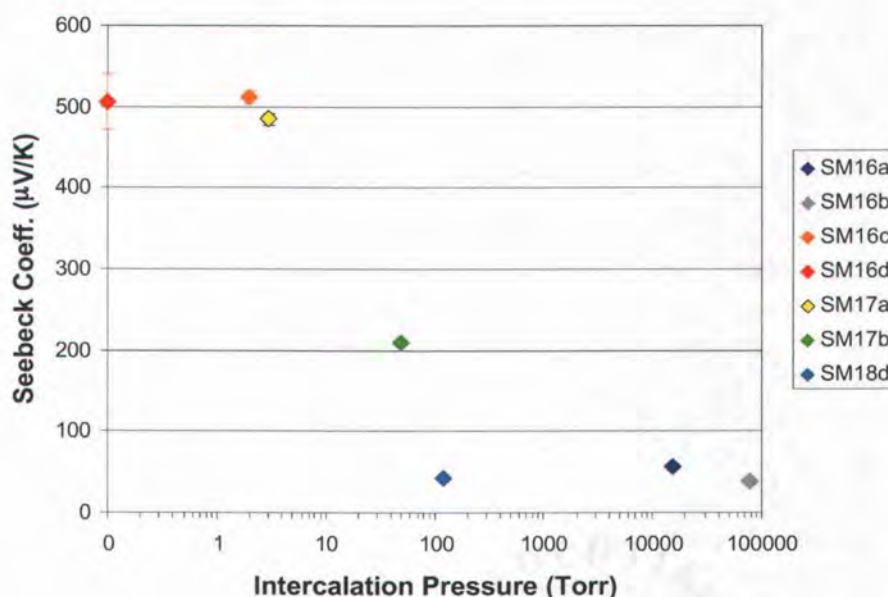


Figure 6.11 Pressure data for  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  samples

Langmuir's model for surface adsorption considers the bound system (copper layer) and the free gas (oxygen) to be in thermal equilibrium. Thus, the thermodynamic model follows the same assumptions as examined in Chapter 4 for the least-biased model. An essential element of Langmuir's model is the definition of the parameter  $\rho$ ,



representing the fraction of occupied sites, which is the fraction of gas particles out of the total number of available sites [23]. In our cases, this is precisely the concentration parameter,  $\rho = N_o/N_{Cu}$ . The key feature of Langmuir's model is that the fractional site occupation parameter is correlated to the pressure [23] at which the surface adsorption occurs,

$$\rho = \frac{P}{\Pi_0 + P}. \quad (6.26)$$

Here,  $P$  is the pressure and  $\Pi_0$  is a temperature-dependent factor known as the Langmuir isotherm [23], defined as

$$\Pi_0 = n_Q e^{\beta \tilde{\epsilon}} / \beta. \quad (6.27)$$

Here  $\tilde{\epsilon}$  is a surface binding energy parameter of Langmuir's model, not to be confused with the binding energy  $\epsilon$  introduced earlier. The  $n_Q$  parameter is the quantum concentration, a function of the mass of the oxygen gas molecule,  $m$

$$n_Q = \left( \frac{m}{2\pi\beta\hbar^2} \right)^{3/2}. \quad (6.28)$$

Since  $\Pi_0$  depends on numerical constants as well as the mass of the gas molecule, which in our case is oxygen, one expects  $\Pi_0$  to be constant for all samples. Thus, (6.26) is used to examine the correlation,  $\Pi_0$ , between the oxygen interaction pressures and the theoretical parameter  $\rho$  plotted in Figure 6.7.

Solving (6.26) for  $\Pi_0$  as a function of pressure and the concentration parameter  $\rho$  yields

$$\Pi_0 = \frac{P(1-\rho)}{\rho}. \quad (6.29)$$

Using this equation, an estimate of  $\Pi_0$  was calculated for each sample shown in



Figure 6.6. The results of these calculations are shown in the following table.

| Sample | Intercalation Pressure (Torr) | $\rho$ | $\Pi_0$ |
|--------|-------------------------------|--------|---------|
| SM18d  | 120                           | 0.563  | 93.1    |
| SM17b  | 50                            | 0.350  | 92.9    |
| SM16c  | 2                             | 0.021  | 93.2    |

Table 6.1 Langmuir model results

The Langmuir results demonstrate that the  $\Pi_0$  parameter is in fact remaining amazingly constant.

## 6.5 Conclusions

There are two main conclusions to the problem examined in Chapter 6. The first conclusion results from the comparison of the theoretical data to the experimental data in Figure 6.7. This plot demonstrates that the binding energy,  $\epsilon$ , decreases as the intercalated atom concentration,  $\rho$ , increases. We conclude that this is due to the formation of an oxygen band. As the number of intercalated atoms increases, the energy levels of the oxygen atoms overlap causing the formation of an oxygen band. Thus the energy difference between the binding energy of the oxygen and copper atoms, which we defined as  $\epsilon$ , will decrease as the band widens.

The second conclusion results from the analysis of the Langmuir model of surface adsorption applied to the copper layer in  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ . This analysis demonstrates that the Langmuir isotherm parameter remains amazingly constant for the three theoretical cases examined in Figure 6.7, identifying the correlation between the intercalation pressure of the samples and the intercalated atom concentration,  $\rho$ . This conclusion not only provides the context that gives  $\rho$  meaning, but also validates the numeric values calculated for  $\rho$ .

## 7 CONCLUSION

This thesis examines the Seebeck coefficient in the high temperature limit, by first examining familiar thermocouple theory and Boltzmann theory to ease the transition between the common “engineering” interpretation of the Seebeck effect, and the computationally more intensive thermodynamic approach to the Seebeck effect. The latter is explored for narrow-band materials, with carriers whose transport mechanism is hopping, using an approach based on a grand partition function containing Hubbard Hamiltonian interaction terms. The motivation for this work is a publication by P. M. Chaikin and G. Beni that uses a combinatoric approach for calculating the Seebeck coefficient under these conditions. Their approach emphasizes the relationship between entropy and the Seebeck coefficient and yields results for the Seebeck coefficient as a function of a concentration parameter.

Chaikin and Beni’s work is limited by a degeneracy calculation based on possible configurations of electrons on sites. Their approach does not contain any other physical parameters explicitly. Thus, I examined an approach for calculating the Seebeck coefficient for these narrow-band, hopping systems that is based on a grand partition function containing Hubbard Hamiltonian interaction terms. This method emphasizes (1) that the problem is one of maximizing entropy by considering the case of least-bias, and (2) the fundamental relationship between the Seebeck coefficient and the chemical potential.

The transfer matrix approach is examined as an alternate method for obtaining the grand partition function. This method is used to consider both on-site and nearest-neighbor interactions for a Hubbard chain. Examination of results in limiting cases, specifically those of zero or infinite interactions, agree with those calculated in literature using a combinatoric approach.

The least-bias approach is applied to the two-atom system and a special case of the

material  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ , yielding two important outcomes. First, it is determined that the binding energy,  $\epsilon$ , decreases as the intercalated atom concentration,  $\rho$ , increases, most likely due to the formation of an oxygen band. The second important outcome of this chapter is that the Langmuir model of surface adsorption can be applied to this problem, treating the intercalated oxygen atoms as free gas in thermal equilibrium with the copper layer (“surface”). This analysis demonstrates that a correlation exists between the intercalation pressure of the samples and the intercalated atom concentration. This conclusion provides a context for interpreting the concentration parameter,  $\rho$ , that originated in the least-biased approach. Additionally, the Langmuir analysis validates the numeric values calculated for  $\rho$  in Figure 6.7.

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## **APPENDICES**

### A. Seebeck Effect, Classical Argument

In theory, a Seebeck voltage exists across any sample of material with a temperature difference maintained at the ends, as shown in Figure 2.2, repeated here as Figure A.1.

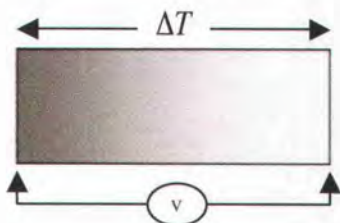


Figure A.1 Seebeck voltage, material

The thermoelectric effect within a material such as that shown in Figure A.1 is often described somewhat classically. Typically, the following discussion is used to describe the thermoelectric effect within metals, but it is also valid for semiconducting materials. As one end of the sample is heated, carriers with charge  $q$  on the hot end of the sample acquire energy. These charge carriers then diffuse toward the cold end of the sample for the following two reasons. One reason is the diffusion process itself, which, according to the second law of thermodynamics, causes the system to proceed to a state of higher entropy. The second reason the charge carriers diffuse toward the cold end is that this state is more energetically favorable. Figure A.2 shows this process for an n-type material, where by definition the charge carriers are electrons.



Figure A.2 N-type example; Thermally energetic charge carriers diffuse toward the cold end of the sample

This diffusion process results in an accumulation of charge carriers at the cold end of the sample, and an accumulation of oppositely charged ions at the hot end of the

sample. This establishes an electric field, which by definition is in the direction from positive charge to negative charge. This direction will either be *hot*  $\rightarrow$  *cold* or *cold*  $\rightarrow$  *hot*, depending on whether the charge carriers are electrons or holes, respectively. An example of this effect for an n-type material and a p-type material are shown in Figure A.3 and Figure A.4, respectively.

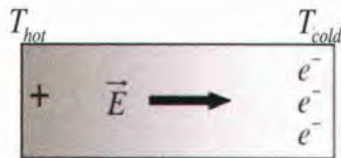


Figure A.3 N-type example. Electric field established



Figure A.4 P-type example. Electric field established

Thus, charge carriers urged to move due to the thermal gradient will also feel a repulsive effect from this electric field established within the sample, creating a state of “dynamic equilibrium” [8]. This means that the flux of carriers in both directions is equal. However, the charge carriers at the hot end will have higher velocities with respect to those at the cold end, which ensures that heat will continue to transfer [8]. This is the basis for the thermoelectric effect. The fact that there is no net flux of carriers means there is no actual charge transfer during this equilibrium state. The fact that the current is zero for this effect will be important for the first principles derivation of the Seebeck effect, discussed in Chapter 2.

The voltage that is induced by the electric field is called the Seebeck voltage. The Seebeck coefficient<sup>1</sup>,  $S$ , can then be calculated from

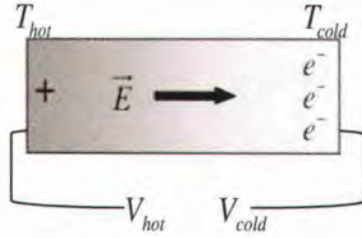
<sup>1</sup> In practice, the symbols  $S$  and  $\alpha$  are most commonly used to represent the Seebeck coefficient.



$$S = - \left( \frac{V_{hot} - V_{cold}}{T_{hot} - T_{cold}} \right), \quad (A.1)$$

which is a modification of (2.1) [19]. Note that the denominator  $\Delta T = T_{hot} - T_{cold}$  will always be positive since  $T_{hot} > T_{cold}$ , thus the sign of the Seebeck coefficient is determined by  $\Delta V = V_{hot} - V_{cold}$ . One usually sees (A.1) written in the following form without regard to the sign convention,  $S = \Delta V / \Delta T$ .

As discussed in Chapter 2 of this paper, the Seebeck coefficient is positive if the carriers are holes and negative if the carriers are electrons. For example, consider measuring the Seebeck voltage for the n-type sample shown in Figure A.5.



**Figure A.5 Measuring the Seebeck voltage**

Here,  $V_{hot} > V_{cold}$  so  $\Delta V = V_{hot} - V_{cold} > 0$ . Since the denominator of (A.1) is always positive, this means that the Seebeck coefficient given by (A.1) will be negative, thus verifying that the sample is n-type.

In practice, the Seebeck voltage for this sample cannot be measured directly since a voltmeter and leads must also be attached to the material. This must be accounted for when calculating the Seebeck coefficient. In this case, the Seebeck coefficient determined by (A.1) would correspond to a total Seebeck coefficient for the sample-leads system,

$$\alpha_{system} = - \left( \frac{V_{hot} - V_{cold}}{T_{hot} - T_{cold}} \right). \quad (A.2)$$

The Seebeck coefficient for the sample alone may be calculated, assuming the composition of the leads is known. The Seebeck coefficient for the entire system is just the difference of the coefficient for the sample and leads,

$$\alpha_{system} = \alpha_{sample} - \alpha_{leads}. \quad (A.3)$$

In the case of the n-type example described earlier, suppose copper leads were used to measure the Seebeck voltage. The Seebeck coefficient for copper at room temperature is approximately  $2\mu V/K$ , thus one would add  $2\mu V/K$  to the system's Seebeck coefficient to determine the Seebeck coefficient for the sample [1]. One method for deriving the form shown in (A.3) is by examining the Seebeck coefficient of a differential thermocouple, as described in Appendix B.

The form of (A.3) follows the convention of

$$\alpha_{AB} = \alpha_A - \alpha_B, \quad (A.4)$$

which is usually used for Type AB differential thermocouples.

## B. Differential Thermocouple

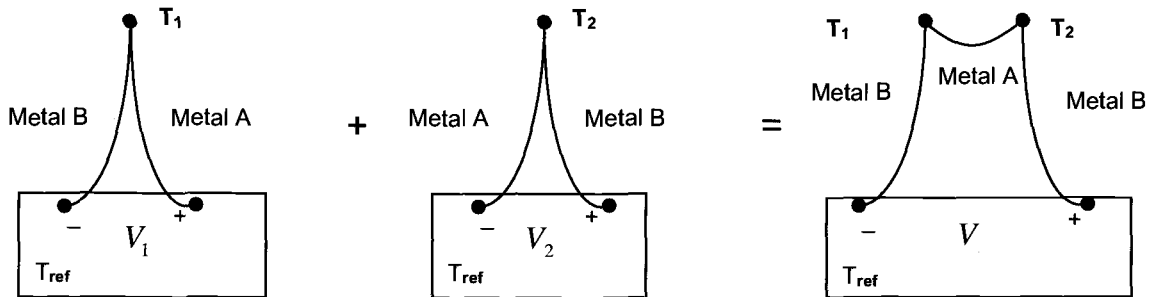
The expression for the Seebeck coefficient of a system composed of a sample and leads is given in Appendix A, and repeated here

$$\alpha_{system} = \alpha_{sample} - \alpha_{leads}. \quad (B.1)$$

The expression (B.1) follows the subscript convention,

$$\alpha_{AB} = \alpha_A - \alpha_B. \quad (B.2)$$

The basis for this convention can be understood by examining the Seebeck coefficient of a differential thermocouple. One method for examining the theory of a differential thermocouple is to examine the addition of two single thermocouples, as follows.



**Figure B.1 Type BAB Differential Thermocouple**

Here, the sum of the two single thermocouple schematics at the left of the figure represents the differential thermocouple schematic shown at the right of the figure. The two single thermocouple schematics represent a Type *BA* and a Type *AB* thermocouple, with junctions being heated to  $T_1$  and  $T_2$ , respectively. The Seebeck voltages of each single thermocouple are measured at a reference temperature,  $T_{ref}$ . It is assumed that  $T_1 > T_2 > T_{ref}$ .

Note that the schematic of the differential thermocouple is the same as that for a “material and leads” system shown in Figure A.5, where metal  $A$  represents the sample and metal  $B$  represents the leads. Metals  $A$  and  $B$  will have absolute Seebeck coefficients of  $\alpha_A$  and  $\alpha_B$  respectively. Furthermore, the differential thermocouple used in experiment has some Seebeck coefficient  $\alpha_{DTC}$ , and the corresponding Seebeck voltage,  $V$ , must be given by

$$V = \alpha_{DTC}(T_1 - T_2). \quad (B.3)$$

The theory describing a differential thermocouple is derived from the addition of two single thermocouples, as shown in Figure B.1. This step follows because the voltage between two ends depends only on the difference in the end temperature and is therefore path independent. Thus, we can solve for the Seebeck voltage  $V$  in terms of  $V_1$  and  $V_2$  in Figure B.1. Comparing this result with (B.3) should yield an expression for  $\alpha_{DTC}$ .

Following the convention that  $V = V_+ - V_-$ , both  $V_1$  and  $V_2$  in Figure B.1 can be determined as follows,

$$V_{1-} = \alpha_B(T_1 - T_{ref}) \quad (B.4)$$

$$V_{1+} = \alpha_A(T_1 - T_{ref}) \quad (B.5)$$

$$V_{2-} = \alpha_A(T_2 - T_{ref}) \quad (B.6)$$

$$V_{2+} = \alpha_B(T_2 - T_{ref}) \quad (B.7)$$

$$V_1 = V_{1+} - V_{1-} = (\alpha_A - \alpha_B)(T_1 - T_{ref}) \quad (B.8)$$

$$V_2 = V_{2+} - V_{2-} = (\alpha_B - \alpha_A)(T_2 - T_{ref}). \quad (B.9)$$

Similarly, one can determine  $V$  in terms of  $\alpha_A$  and  $\alpha_B$ ,

$$V = V_1 + V_2 = (\alpha_A - \alpha_B)(T_1 - T_{ref}) + (\alpha_B - \alpha_A)(T_2 - T_{ref}) \quad (B.10)$$

$$V = (\alpha_A - \alpha_B)(T_1 - T_{ref} - T_2 + T_{ref}) \quad (B.11)$$

$$V = (\alpha_A - \alpha_B)(T_1 - T_2). \quad (B.12)$$

Applying the convention given by (B.2), (B.12) simplifies to

$$V = \alpha_{AB}(T_1 - T_2). \quad (B.13)$$

Thus, for a BAB differential thermocouple,  $\alpha_{DTC}$  in (B.3) can be replaced by  $\alpha_{AB}$ .

This relates to the “sample and leads” problem as follows. Recall that the differential thermocouple, shown at the right of Figure B.1, is identical to the sample-leads system, shown in Figure A.5, where metals  $A$  and  $B$  have been replaced by the sample and leads, respectively. Thus, the following substitutions are made,

$$\begin{aligned} \alpha_{AB} &\rightarrow \alpha_{system} \\ \alpha_A &\rightarrow \alpha_{sample} \\ \alpha_B &\rightarrow \alpha_{leads} \end{aligned} \quad (B.14)$$

Using these substitutions, the convention shown in (B.2) becomes

$$\alpha_{system} = \alpha_{leads} - \alpha_{sample}. \quad (B.15)$$

Additionally, (B.13) can also be used to validate (A.2). The Seebeck voltage measured for the differential thermocouple is  $V = V_+ - V_-$ . Applying this substitution to (B.13) and solving for the Seebeck coefficient for the system yields

$$\alpha_{AB} = \frac{V_+ - V_-}{T_1 - T_2}. \quad (B.16)$$

Since  $T_1 > T_2$  in Figure B.1, the following substitutions are made,

$$\begin{aligned}
T_1 &\rightarrow T_{Hot} \\
T_2 &\rightarrow T_{Cold} \\
V_- &\rightarrow V_{Hot} \\
V_+ &\rightarrow V_{Cold}
\end{aligned} \tag{B.17}$$

Applying these substitutions to (B.13) yields

$$\alpha_{AB} = - \left( \frac{V_{Hot} - V_{Cold}}{T_{Hot} - T_{Cold}} \right), \tag{B.18}$$

which precisely matches (A.2).

### C. Boltzmann's Equation

The carriers of a system are typically described by a local occupation function,  $f(\mathbf{r}, \mathbf{k}, t)$ , where  $\mathbf{r}$  is the local spatial coordinate,  $\mathbf{k}$  is the wavenumber of a quantum state and  $t$  is an explicit time dependence. The total differential of  $f$  with respect to  $t$  is given by

$$\frac{df}{dt} = \nabla_{\mathbf{r}} f \cdot \dot{\mathbf{r}} + \nabla_{\mathbf{k}} f \cdot \dot{\mathbf{k}} + \frac{\partial f}{\partial t}. \quad (\text{C.1})$$

In equilibrium, the function does not evolve in time, thus

$$\frac{df}{dt} = 0 \quad (\text{C.2})$$

and  $f(\mathbf{r}, \mathbf{k}, t)$  is given by the Fermi distribution function  $f_o(\epsilon)$ ,

$$f_o(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}, \quad (\text{C.3})$$

where  $\epsilon(k) = \hbar^2 k^2 / 2m$  is the energy of the carrier,  $\mu$  is the chemical potential, and  $\beta = 1/k_B T$  where  $k_B$  is Boltzmann's constant and  $T$  is temperature. In the non-equilibrium case where the distribution function does evolve in time,

$$\frac{df}{dt} \neq 0. \quad (\text{C.4})$$

The non-equilibrium case allows for carrier transport, defined by the net result of scattering processes. These scattering processes are caused by carrier interactions with other particles or potentials, and can be described by quantum transitions to and from a quantum state  $\mathbf{k}$ ,

$$\mathbf{k} \rightarrow \mathbf{k}' \quad (\text{C.5})$$

$$\mathbf{k}'' \rightarrow \mathbf{k} \quad (\text{C.6})$$

Boltzmann theory describes the time evolution of  $f(\mathbf{r}, \mathbf{k}, t)$  by equating the right hand side of (C.1) to the change in  $f$  due to scattering,

$$\frac{df}{dt} = \left( \frac{df}{dt} \right)_{\text{scattering}} \quad (\text{C.7})$$

$$\nabla_r f \cdot \dot{\mathbf{r}} + \nabla_k f \cdot \dot{\mathbf{k}} + \frac{\partial f}{\partial t} = \left( \frac{df}{dt} \right)_{\text{scattering}}. \quad (\text{C.8})$$

It is then assumed that scattering is weak, such that the rate at which the distribution function returns to the equilibrium position due to scattering is proportional to the deviation of  $f$  from  $f_o$ . This is called the relaxation approximation and is described by [9]

$$\left( \frac{df}{dt} \right)_{\text{scatt}} = -\frac{f - f_o}{\tau}, \quad (\text{C.9})$$

where  $\tau$  is the relaxation time [25]. Substituting (C.9) into (C.8) yields Boltzmann's equation within the relaxation time approximation,

$$\nabla_r f \cdot \dot{\mathbf{r}} + \nabla_k f \cdot \dot{\mathbf{k}} + \frac{\partial f}{\partial t} = -\frac{f - f_o}{\tau}. \quad (\text{C.10})$$

Although an exact solution to Boltzmann's equation is difficult to achieve, an approximate solution can be found by considering the following two approximations. First, only small deviations from equilibrium will be considered, i.e. weak scattering, such that  $|f - f_o| \ll f_o$ , thus  $f \approx f_o(\epsilon)$  [1]. Additionally, there is no explicit time dependence, thus  $\left( \frac{\partial f}{\partial t} \right) = 0$ . Under these two assumptions, note that the following substitutions can be made,

$$\nabla_k f \cdot \dot{\mathbf{k}} = \frac{\partial f_o}{\partial \epsilon} \nabla_k \epsilon \cdot \dot{\mathbf{k}} \quad (\text{C.11})$$



$$\nabla_r f \cdot \dot{\mathbf{r}} = \frac{\partial f_o}{\partial \beta} \nabla_r \beta \cdot \dot{\mathbf{r}} + \frac{\partial f_o}{\partial \mu} \nabla_r \mu \cdot \dot{\mathbf{r}}. \quad (\text{C.12})$$

Making the following substitutions,

$$\frac{\partial f_o}{\partial \beta} = (\varepsilon - \mu) \frac{1}{\beta} \frac{\partial f_o}{\partial \varepsilon} \quad (\text{C.13})$$

$$\frac{\partial f_o}{\partial \mu} = -\frac{\partial f_o}{\partial \varepsilon}, \quad (\text{C.14})$$

yields a revised expression for (C.12),

$$\nabla_r f \cdot \dot{\mathbf{r}} = (\varepsilon - \mu) \frac{1}{\beta} \frac{\partial f_o}{\partial \varepsilon} \nabla_r \beta \cdot \dot{\mathbf{r}} - \frac{\partial f_o}{\partial \varepsilon} \nabla_r \mu \cdot \dot{\mathbf{r}}. \quad (\text{C.15})$$

Furthermore, note the following substitutions can be made,

$$\dot{\mathbf{r}} = \mathbf{v} = \frac{1}{\hbar} \nabla_k \varepsilon(\mathbf{k}) \quad (\text{C.16})$$

$$\hbar \dot{\mathbf{k}} = q \left( \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{H} \right). \quad (\text{C.17})$$

In this approximation however, only weak scattering is considered. Thus, for only small deviations from equilibrium, consider the fields to be negligible,  $\hbar \dot{\mathbf{k}} \rightarrow 0$ .

Applying these substitutions yields an approximation for (C.10),

$$-\frac{1}{\hbar} \nabla_k \varepsilon \frac{\partial f_o}{\partial \varepsilon} \left[ (\varepsilon - \mu) \frac{1}{\beta} \nabla_r \beta - \nabla_r \mu \right] = \frac{f - f_o}{\tau}. \quad (\text{C.18})$$

Note that the one-dimensional approximation for (C.18) is as follows,

$$v_x \frac{\partial f_o}{\partial \varepsilon} \left[ \frac{(\varepsilon - \mu)}{T} \frac{\partial T}{\partial x} + \frac{\partial \mu}{\partial x} \right] = \frac{f - f_o}{\tau}. \quad (\text{C.19})$$

#### D. Method of Lagrange Multipliers Applied to Seebeck Problem

The Lagrangian is formed according to the method of Lagrange multipliers. The function to be maximized is the “fairness” function, which represents entropy, as described in Chapter 4. According to the method of Lagrange multipliers, the constraints must be constructed such that they equal constant values. Thus, the second term of the Lagrangian is the constraint that the sum of the probabilities must equal one. Although it will not be evident until we are further into the method of Lagrange multipliers, the second term could equivalently be written as the following, without affecting the outcome:  $-\lambda_o \sum_{N=0,1,2,\dots} \mathcal{P}[E_s(N)] - 1$ . The final term is the constraint that the expectation value for the thermodynamic Hamiltonian, which by definition is a measured observable, must be equal to a constant. Similar to the first constraint, this second constraint could equivalently be written as  $\lambda_1 \left\langle \hat{\mathcal{H}} \right\rangle - c$ . Thus, there are two constraints and we let the Lagrange multipliers be  $\lambda_o$  and  $\lambda_1$ . Using these constraints, the Lagrangian is given by

$$\begin{aligned} \mathcal{L} = & -k_B \sum_{N=0,1,2,\dots} \mathcal{P}[E_s(N)] \log \mathcal{P}[E_s(N)] \\ & - \lambda_o \sum_{N=0,1,2,\dots} \mathcal{P}[E_s(N)] - \lambda_1 \left\langle \hat{\mathcal{H}} \right\rangle \end{aligned} \quad (D.1)$$

Note that the last term in the Lagrangian is the expectation value for the grand canonical Hamiltonian, which can be put in terms of the expectation values of  $\mathcal{H}_{op}$  and  $\mathcal{N}_{op}$  using (4.11). Making this substitution into (D.1) yields the Lagrangian

$$\begin{aligned} \mathcal{L} = & -k_B \sum_{N=0,1,2,\dots} \mathcal{P}[E_s(N)] \log \mathcal{P}[E_s(N)] - \lambda_o \sum_{N=0,1,2,\dots} \mathcal{P}[E_s(N)] \\ & - \lambda_1 \left\{ \sum_{N=0,1,2,\dots}^s E_s(N) \mathcal{P}[E_s(N)] - \mu \sum_{N=0,1,2,\dots}^s N \mathcal{P}[E_s(N)] \right\} \end{aligned} \quad (D.2)$$

## E. Ising Model

The purpose of the Ising model is to examine a system of interacting atoms. The one dimensional Ising model is called an Ising chain, and has an exact solution. This chain consists of  $N$  atoms, and can either have free ends, or periodic conditions such that a circular chain exists. Oftentimes, magnetic systems are modeled this way, and the interaction of the atoms' magnetic moments can be described in terms of the electron spin interactions [26].

For example, let  $J$  be the magnitude of the interaction between nearest-neighbor atoms in a chain of length  $N$  with free ends. For simplicity, only electron spin in the  $z$  direction is considered, thus let spin-up and spin-down be represented by  $\sigma_i = \pm 1$ . The sum of these interactions will then be the Hamiltonian of the system,  $H$ ,

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}. \quad (\text{E.1})$$

The partition function for the system is found by substituting the Hamiltonian into the following equation [26]

$$Z_N = \sum_{\sigma_1 = \pm 1} \dots \sum_{\sigma_N = \pm 1} e^{-\beta H}. \quad (\text{E.2})$$

Here,  $\beta = 1/k_B T$  where  $k_B$  is Boltzmann's constant and  $T$  is temperature. Completing this summation yields a closed-form of the partition function,

$$Z_N = 2(2 \cosh \beta J)^{N-1}. \quad (\text{E.3})$$

Additional interactions present within the system are considering by including these terms in the Hamiltonian. For example, if this magnetic system were in the presence of a magnetic field proportional to  $h$ , the Hamiltonian for a periodic chain would be written as follows,

$$H = -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - h \sum_{i=1}^N \sigma_i. \quad (\text{E.4})$$

Again, a partition function for the system is calculated by substituting the Hamiltonian into (E.2). Additional terms in the Hamiltonian complicate the sums in the partition function, and make it difficult to simplify to a closed-form solution. The transfer matrix method is often applied at this point to get the closed form of the partition function.

## F. Mathematica Worksheet for Chapter 6 Calculations, Case A

First, all variables are cleared and the graphics packages are loaded.

```
Clear[μ, μcu, μo, No, Ncu, Uo, λ, β, ε, x, dg, rs, ρ, avgNcu, avgNox, avgNcuλ,
  avgNoxλ, γ, ξgrCu, ξgrO, kBJ, rt]
<< Graphics`Graphics`
<< Graphics`Colors`
```

Then the grand partition functions for electrons on copper sites and oxygen sites are defined, given in Chapter 6 by (6.3) and (6.4).

```
ξgrCu = (1 + 2 E^(β μcu))^Ncu
ξgrO = (1 + 2 E^(-β (ε - μo)) + E^(-β ((2 ε - 2 μo) + Uo)))^No
(1 + 2 E^(β μcu))^Ncu
(1 + E^(-β (Uo + 2 ε - 2 μo)) + 2 E^(-β (ε - μo)))^No
```

Next the average number of electrons on copper sites and oxygen sites are calculated

using expression (4.26),  $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log \mathcal{Z}_{gr}$ . Note that the substitution  $\mu_o = \mu_{Cu}$  is applied, since the chemical potentials must be equivalent in chemical equilibrium. Additionally, the substitution  $e^{-\beta \epsilon} \rightarrow x$  is made to simplify the expression.

```
avgNcu = (1/β) D[Log[ξgrCu], μcu] // Simplify
avgNox = (1/β) D[Log[ξgrO], μo] /. {μo → μcu, ε → (-1/β) Log[x]} // Simplify
(2 E^(β μcu) Ncu) / (1 + 2 E^(β μcu))
(2 No x (E^(β (Uo - μcu)) + x)) / (E^(β (Uo - 2 μcu)) + 2 E^(β (Uo - μcu)) x + x^2)
```

The substitution  $e^{\beta \mu} \rightarrow \lambda$  is applied to simplify the above equations.

```
avgNcuλ = avgNcu /. {μcu → (1/β) Log[λ]}
avgNoxλ = avgNox /. {μcu → (1/β) Log[λ]}
(2 Ncu λ) / (1 + 2 λ)
```

```
(2 No x (E^(β (Uo - Log[λ]/β)) + x)) / (E^(β (Uo - 2 Log[λ]/β)) + 2 E^(β (Uo - Log[λ]/β)) x + x^2)
```

The conservation equation is then defined such that the root will be  $\lambda$ , and the substitution,  $e^{-\beta U_0} \rightarrow y$ , is made to simplify the expression. The intercalated atom concentration parameter,  $\rho$ , defined in Chapter 6 by (6.10) is also introduced in this step.

$$\mathbf{dg} = (\mathbf{avgNcu}\lambda + \mathbf{avgNox}\lambda - \mathbf{Ncu}) / \{ \mathbf{No} \rightarrow \rho \mathbf{Ncu}, \mathbf{Uo} \rightarrow (-1/\beta) \mathbf{Log}[y] \} // \mathbf{Simplify}$$

$$\frac{\mathbf{Ncu} (-1 + 2 x \lambda (-1 + \rho + 2 \lambda \rho) + x^2 y \lambda^2 (-1 + (2 + 4 \lambda) \rho))}{(1 + 2 \lambda) (1 + 2 x \lambda + x^2 y \lambda^2)}$$

The conservation equation is to third order in  $\lambda$ , thus three roots are expected.

$$\mathbf{rt} = \lambda /. \mathbf{Solve}[\mathbf{dg} == 0, \lambda]$$

$$\left\{ -\frac{x^2 y + 4 x \rho + 2 x^2 y \rho}{12 x^2 y \rho} - \frac{(24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)}{6 \cdot 2^{2/3} x^2 y \rho (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3})^{1/3}} + \frac{1}{12 \cdot 2^{1/3} x^2 y \rho} \left( (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3})^{1/3} \right) - \frac{-x^2 y + 4 x \rho + 2 x^2 y \rho}{12 x^2 y \rho} + \left( (1 + \frac{1}{2} \sqrt{3}) (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2) \right) / \left( 12 \cdot 2^{2/3} x^2 y \rho (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3})^{1/3} \right) - \frac{1}{24 \cdot 2^{1/3} x^2 y \rho} \left( (1 - \frac{1}{2} \sqrt{3}) (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3})^{1/3} \right) \right\}$$

$$\begin{aligned}
& \frac{-x^2 y + 4 x \rho + 2 x^2 y \rho}{12 x^2 y \rho} + \left( (1 - i\sqrt{3}) \left( 24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2 \right) \right) / \\
& \left( 12 2^{2/3} x^2 y \rho \right. \\
& \quad (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + \\
& \quad 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \\
& \quad \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 \\
& \quad x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3} \Big)^{1/3} \Big) - \\
& \frac{1}{24 2^{1/3} x^2 y \rho} \left( (1 + i\sqrt{3}) \left( 2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + \right. \right. \\
& \quad 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \\
& \quad \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 \\
& \quad x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3} \Big)^{1/3} \Big) \Big\}
\end{aligned}$$

One of the three solutions is real, and the other two solutions are complex. The appropriate solution is determined as follows. The Seebeck coefficient is given by  $S = -\mu/qT$ . Therefore, in terms of  $\lambda$ , the Seebeck coefficient is defined as  $S = -\frac{1}{qT} \left( \frac{1}{\beta} \log \lambda \right) = -\frac{k_B}{q} \log \lambda$ . The natural log of a complex number will not yield a real solution for the Seebeck coefficient. Since the Seebeck coefficient is a measurable, the correct  $\lambda$  solution must be real. Thus,  $\lambda$  is defined as a real function of the concentration parameter as follows.

$$\mathbf{rs} = \mathbf{rt}[[1]]$$

$$\begin{aligned}
& \frac{-x^2 y + 4 x \rho + 2 x^2 y \rho}{12 x^2 y \rho} - \\
& \left( 24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2 \right) / \left( 6 2^{2/3} x^2 y \rho (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + \right. \\
& \quad 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \\
& \quad \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 \\
& \quad x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3} \Big)^{1/3} \Big) + \\
& \frac{1}{12 2^{1/3} x^2 y \rho} \left( (2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + \right. \\
& \quad 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3 + \\
& \quad \sqrt{(2 x^6 y^3 + 48 x^5 y^2 \rho - 12 x^6 y^3 \rho - 192 x^4 y \rho^2 + 432 x^4 y^2 \rho^2 - 120 x^5 y^2 \rho^2 + 24 x^6 y^3 \rho^2 - 128 x^3 \rho^3 + \\
& \quad 96 x^4 y \rho^3 + 48 x^5 y^2 \rho^3 - 16 x^6 y^3 \rho^3)^2 + 4 (24 x^2 y \rho (-x + x \rho) - (-x^2 y + 4 x \rho + 2 x^2 y \rho)^2)^3} \Big)^{1/3} \Big)
\end{aligned}$$

At this point, the substitutions  $e^{-\beta \epsilon} \rightarrow x$ ,  $e^{\beta \mu} \rightarrow \lambda$  and  $e^{-\beta U_0} \rightarrow y$  are removed so that the solution is in terms of the original parameters. Additionally, numerical values for Boltzmann's constant are applied so that a numerical solution of the Seebeck coefficient can be examined. Since electron occupations are considered in this problem,  $q$  is defined as the charge of an electron. Parameters are chosen in the

appropriate units such that the binding energy and on-site Coulomb energy are given in units  $eV$ , and the Seebeck coefficient solution is given in units  $\mu V/K$ . The oxygen binding energy is defined relative to the copper binding energy, as given by the expression (6.12) in Chapter 6.

```
x = Exp[-ε / (kB T)]
y = Exp[-Uo / (kB T)]
kB = 8.6 10^-5
kBj = 1.38062 10^(-23)
q = -1.60219 10^(-19)
S = -(kBj 10^6 / q) Log[rs]:
```

$$\exp\left\{-\frac{\epsilon}{k_B T}\right\}$$

$$\exp\left\{-\frac{U_o}{k_B T}\right\}$$

0.000086

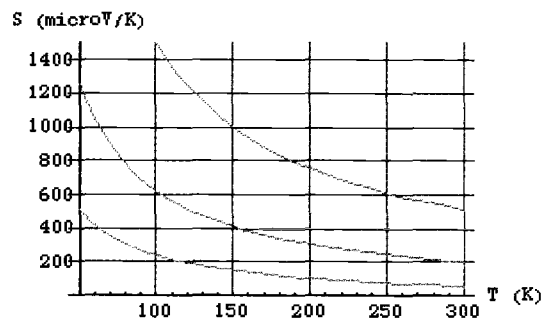
$1.38062 \times 10^{-23}$

$-1.60219 \times 10^{-19}$

The above step also defines the function for the Seebeck coefficient,  $S = -\frac{k_B}{q} \log \lambda$ .

Numeric results for the Seebeck coefficient can then be plotted for various values of  $\epsilon$ ,  $\rho$  and  $U_o$ .

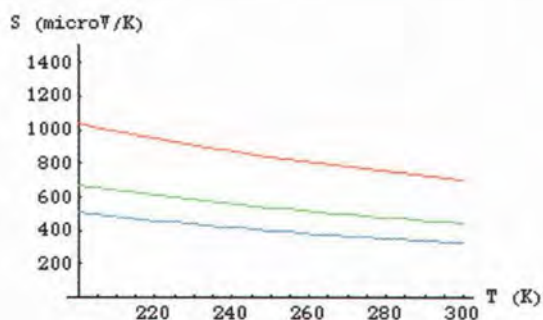
```
<< Graphics`Legend`
p1 = Plot[S /. {ε → 0.4, Uo → -0.36, ρ → 0.1}, {T, 50, 300}, PlotStyle → {Red},
  PlotRange → {0, 1500}];
p2 = Plot[S /. {ε → 0.275, Uo → -0.36, ρ → 0.35}, {T, 50, 300}, PlotStyle → {Green},
  PlotRange → {0, 1500}];
p3 = Plot[S /. {ε → 0.22, Uo → -0.36, ρ → 0.65}, {T, 50, 300}, PlotStyle → {Blue},
  PlotRange → {0, 1500}];
t1 = Show[p1, p2, p3, GridLines → Automatic, AxesLabel → {"T (K)", "S (microV/K)"}]
```





The Seebeck coefficient was also examined for positive values of the oxygen on-site Coulomb interaction.

```
<< Graphics`Legend`
p4 = Plot[S /. { $\epsilon \rightarrow 0.4$ ,  $U_o \rightarrow 0$ ,  $\rho \rightarrow 0.1$ }, {T, 200, 300}, PlotStyle -> {Red},
  PlotRange -> {0, 1500}];
p5 = Plot[S /. { $\epsilon \rightarrow 0.275$ ,  $U_o \rightarrow +0.01$ ,  $\rho \rightarrow 0.35$ }, {T, 200, 300}, PlotStyle -> {Green},
  PlotRange -> {0, 1500}];
p6 = Plot[S /. { $\epsilon \rightarrow 0.22$ ,  $U_o \rightarrow +0.1$ ,  $\rho \rightarrow 0.65$ }, {T, 200, 300}, PlotStyle -> {Blue},
  PlotRange -> {0, 1500}];
t2 = Show[p4, p5, p6, AxesLabel -> {"T (K)", "S (microV/K)"}]
```



Data sets can also be generated in this Mathematica worksheet, for use in Excel. Data tables are defined and exported as comma-separated-value files.

```
data = Table[S /. { $\epsilon \rightarrow 0.4$ ,  $U_o \rightarrow -0.36$ ,  $\rho \rightarrow 0.1$ }, {T, 50, 300, 5}]
Export["red.csv", data, "CSV"]
data = Table[S /. { $\epsilon \rightarrow 0.275$ ,  $U_o \rightarrow -0.36$ ,  $\rho \rightarrow 0.35$ }, {T, 50, 300, 5}]
Export["green.csv", data, "CSV"]
data = Table[S /. { $\epsilon \rightarrow 0.22$ ,  $U_o \rightarrow -0.36$ ,  $\rho \rightarrow 0.65$ }, {T, 50, 300, 5}]
Export["blue.csv", data, "CSV"]

{2965.48, 2698.28, 2475.62, 2287.21, 2125.72, 1985.76, 1863.29, 1755.24, 1659.19, 1573.25, 1495.9,
  1425.92, 1362.3, 1304.21, 1250.97, 1201.98, 1156.76, 1114.89, 1076.02, 1039.82, 1006.03,
  974.429, 944.798, 916.963, 890.765, 866.064, 842.734, 820.665, 799.757, 779.92, 761.075,
  743.148, 726.074, 709.794, 694.253, 679.402, 665.196, 651.594, 638.559, 626.054, 614.05,
  602.515, 591.424, 580.75, 570.472, 560.566, 551.015, 541.798, 532.898, 524.3, 515.988}

red.csv

{1259.52, 1144.14, 1047.99, 966.63, 896.894, 836.457, 783.575, 736.914, 695.439, 658.329, 624.931,
  594.714, 567.245, 542.165, 519.176, 498.027, 478.506, 460.432, 443.65, 428.027, 413.447,
  399.808, 387.023, 375.015, 363.714, 353.06, 342.999, 333.483, 324.47, 315.92, 307.799,
  300.075, 292.72, 285.708, 279.016, 272.623, 266.508, 260.655, 255.046, 249.667, 244.504,
  239.544, 234.775, 230.187, 225.77, 221.513, 217.41, 213.45, 209.627, 205.935, 202.365}

green.csv

{506.938, 458.349, 417.855, 383.587, 354.209, 328.743, 306.455, 286.784, 269.294, 253.639, 239.546,
  226.789, 215.188, 204.592, 194.875, 185.931, 177.671, 170.02, 162.913, 156.292, 150.11,
  144.325, 138.898, 133.798, 128.996, 124.466, 120.186, 116.135, 112.296, 108.652, 105.189,
  101.893, 98.7524, 95.7567, 92.8958, 90.1607, 87.5434, 85.0362, 82.6323, 80.3253, 78.1096,
  75.9796, 73.9304, 71.9575, 70.0566, 68.2238, 66.4554, 64.748, 63.0984, 61.5038, 59.9613}

blue.csv
```

## G. Mathematica Worksheet for Chapter 6 Calculations, Case B

This worksheet follows the same steps as Case A examined in Appendix F. The difference is that Case B eliminates the option of single occupancy on the oxygen site, thus there is no on-site Coulomb interaction  $U_o$  in the oxygen grand partition function.

```

Clear[μ, μcu, μo, No, Ncu, Uo, λ, β, ε, x, dg, rs, ρ, avgNcu, avgNox, avgNcuλ,
  avgNoxλ, γ, ζgrCu, ζgrO, kBJ, rt]
<< Graphics`Graphics`
<< Graphics`Colors`

ζgrCu = (1 + 2 E^(β μcu))^Ncu
ζgrO = (1 + E^(-2 β (ε - μo)))^No

(1 + 2 e^(β μcu))^Ncu
(1 + e^(-2 β (ε - μo)))^No

avgNcu = (1/β) D[Log[ζgrCu], μcu] // Simplify
avgNox = (1/β) D[Log[ζgrO], μo] /. {μo → μcu, ε → (-1/β) Log[x]} // Simplify


$$\frac{2 e^{\beta \mu_{cu}} N_{cu}}{1 + 2 e^{\beta \mu_{cu}}}$$



$$\frac{2 N_o}{1 + e^{-2 (\beta \mu_{cu} + \text{Log}[x])}}$$


avgNcuλ = avgNcu /. {μcu → (1/β) Log[λ]}
avgNoxλ = avgNox /. {μcu → (1/β) Log[λ]}


$$\frac{2 N_{cu} \lambda}{1 + 2 \lambda}$$



$$\frac{2 N_o}{1 + e^{-2 (\text{Log}[x] + \text{Log}[\lambda])}}$$


dg = avgNcuλ + avgNoxλ - Ncu /. {No → ρ Ncu} // Simplify

Ncu \left( -1 + \frac{2 \lambda}{1 + 2 \lambda} + \frac{2 \rho}{1 + \frac{1}{x^2 \lambda^2}} \right)

```

Again, since the equation is to the third order in  $\lambda$ , there will be three roots for the above expression. Just as for Case A, there are two complex solutions and one real solution.

$$\mathbf{rt} = \lambda /. \text{Solve}[\mathbf{dg} == 0, \lambda]$$

$$\left\{ -\frac{-x^2 + 2x^2\rho}{12x^2\rho} + \frac{(-x^2 + 2x^2\rho)^2}{12x^2\rho \left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3}} + \frac{\left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3}}{12x^2\rho} \right. \\ \left. - \frac{-x^2 + 2x^2\rho}{12x^2\rho} - \frac{(1 + i\sqrt{3})(-x^2 + 2x^2\rho)^2}{24x^2\rho \left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3}} \right. \\ \left. - \frac{1}{24x^2\rho} \left( (1 - i\sqrt{3}) \left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3} \right. \right. \\ \left. \left. - \frac{-x^2 + 2x^2\rho}{12x^2\rho} - \frac{(1 - i\sqrt{3})(-x^2 + 2x^2\rho)^2}{24x^2\rho \left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3}} \right. \right. \\ \left. \left. - \frac{1}{24x^2\rho} \left( (1 + i\sqrt{3}) \left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3} \right) \right\}$$

The real solution is selected since this will yield a real expression for the Seebeck coefficient.

$$\mathbf{rs} = \mathbf{rt}[[1]]$$

$$-\frac{-x^2 + 2x^2\rho}{12x^2\rho} + \frac{(-x^2 + 2x^2\rho)^2}{12x^2\rho \left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3}} + \frac{\left( x^6 - 6x^6\rho + 216x^4\rho^2 + 12x^6\rho^2 - 8x^6\rho^3 + 12\sqrt{3}\sqrt{x^{10}\rho^2 - 6x^{10}\rho^3 + 108x^8\rho^4 + 12x^{10}\rho^4 - 8x^{10}\rho^5} \right)^{1/3}}{12x^2\rho}$$

Numeric values for Boltzmann's constant and the electron charge are inserted, and the equation for the Seebeck coefficient is formed.

```

x = Exp[-ε / (kB T)]
kB = 8.6 10^-5
kBJ = 1.38062 10^-23
q = -1.60219 10^-19
S = -(kBJ 10^6 / q) Log[rs];

```

$$\frac{11627.9 \text{ eV}}{T}$$

0.000086

$1.38062 \times 10^{-23}$

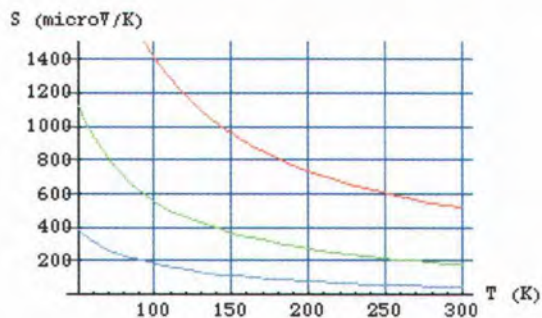
$-1.60219 \times 10^{-19}$

The results are plotted for values of  $\epsilon$  and  $\rho$ .

```

<< Graphics`Legend`
p1 = Plot[S /. {ε → 0.2, ρ → 0.021}, {T, 50, 300}, PlotStyle → {Red},
  PlotRange → {0, 1500}];
p2 = Plot[S /. {ε → 0.085, ρ → 0.35}, {T, 50, 300}, PlotStyle → {Green},
  PlotRange → {0, 1500}];
p3 = Plot[S /. {ε → 0.031, ρ → 0.563}, {T, 50, 300}, PlotStyle → {Blue},
  PlotRange → {0, 1500}];
t1 = Show[p1, p2, p3, GridLines → Automatic, AxesLabel → {"T (K)", "S (microV/K)"}]

```



Data tables are generated and exported as .csv files.

```

dataRed = Table[S /. { $\epsilon \rightarrow 0.2$ ,  $\rho \rightarrow 0.021$ }, {T, 50, 300, 5}]
Export["red.csv", dataRed, "CSV"]
dataGreen = Table[S /. { $\epsilon \rightarrow 0.085$ ,  $\rho \rightarrow 0.35$ }, {T, 50, 300, 5}]
Export["green.csv", dataGreen, "CSV"]
dataBlue = Table[S /. { $\epsilon \rightarrow 0.031$ ,  $\rho \rightarrow 0.563$ }, {T, 50, 300, 5}]
Export["blue.csv", dataBlue, "CSV"]

{2743.11, 2500.2, 2297.78, 2126.5, 1979.69, 1852.46, 1741.12, 1642.89, 1555.57, 1477.44, 1407.13,
1343.51, 1285.68, 1232.87, 1184.46, 1139.93, 1098.83, 1060.76, 1025.42, 992.516, 961.806,
933.077, 906.144, 880.844, 857.034, 834.585, 813.385, 793.332, 774.336, 756.316, 739.199,
722.919, 707.417, 692.639, 678.536, 665.062, 652.178, 639.845, 628.03, 616.702, 605.83,
595.39, 585.355, 575.704, 566.416, 557.47, 548.85, 540.537, 532.516, 524.774, 517.295}

red.csv

{1125.92, 1022.68, 936.656, 863.862, 801.467, 747.393, 700.077, 658.329, 621.22, 588.018, 558.137,
531.103, 506.527, 484.09, 463.524, 444.604, 427.142, 410.974, 395.963, 381.989, 368.949,
356.751, 345.318, 334.579, 324.474, 314.948, 305.953, 297.446, 289.388, 281.746, 274.487,
267.584, 261.012, 254.747, 248.768, 243.056, 237.595, 232.367, 227.359, 222.556, 217.947,
213.52, 209.265, 205.171, 201.231, 197.435, 193.775, 190.245, 186.838, 183.548, 180.368}

green.csv

{390.819, 353.159, 321.772, 295.21, 272.438, 252.699, 235.424, 220.177, 206.622, 194.49, 183.568,
173.685, 164.697, 156.488, 148.962, 142.036, 135.641, 129.718, 124.216, 119.093, 114.31,
109.834, 105.637, 101.693, 97.9808, 94.4795, 91.172, 88.0425, 85.077, 82.263, 79.589,
77.045, 74.6216, 72.3105, 70.1039, 67.995, 65.9774, 64.0453, 62.1933, 60.4166, 58.7107,
57.0714, 55.4948, 53.9775, 52.5162, 51.1078, 49.7494, 48.4385, 47.1727, 45.9495, 44.767}

blue.csv

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