

Thermoelectric Response of Binary Liquid Alloys under Segregation Conditions: A First-Principles Approach

Anuj Anand¹, Dr. Bipasa Raha²

¹Research Scholar, P. G. Department of Physics, Purnea University, Purnia

²Assistant Professor, D. S. College, Katihar

²P.G. Head on Deputation at Department of Physics, Purnea University, Purnia.

Abstract:

Binary liquid alloys exhibit complex thermoelectric behavior arising from compositional disorder, atomic-scale fluctuations, interatomic interactions, and segregation phenomena. This study develops a comprehensive first-principles theoretical framework to investigate the thermoelectric response—particularly the Seebeck coefficient—under segregation conditions. By integrating Boltzmann transport theory with thermodynamic modeling of phase separation, analytical expressions are derived that relate thermopower to the electronic density of states and temperature-dependent chemical potential gradients. The effects of segregation are incorporated through Gibbs free energy minimization and composition-dependent scattering mechanisms, capturing the influence of interaction parameters on transport behavior.

Numerical simulations for representative alloy systems, namely Cu–Bi and Pb–Sn, reveal strong nonlinearity in composition dependence, significant temperature sensitivity, and composition-driven sign reversal of the Seebeck coefficient. The results demonstrate that segregation-induced modifications in electronic structure and carrier scattering play a crucial role in determining thermoelectric performance. These findings provide important insights for the design and optimization of liquid-based thermoelectric materials, with potential applications in liquid metal batteries, high-temperature energy conversion systems, and metallurgical processes.

Keywords: Binary liquid alloys, Seebeck coefficient, segregation, thermoelectric power, first-principles theory, Boltzmann transport, phase separation, Cu–Bi alloy, Pb–Sn alloy.

1. Introduction

Thermoelectric materials, which enable the direct conversion of thermal gradients into electrical energy, have attracted significant attention due to their potential applications in sustainable energy systems, waste heat recovery, and advanced power generation technologies. The fundamental principle underlying thermoelectricity is the Seebeck effect, wherein a temperature difference across a material generates an electric potential (Wikipedia contributors, 2024a). While solid-state thermoelectric materials have been extensively investigated over the past decades, liquid metallic systems remain

comparatively underexplored despite their growing relevance in high-temperature environments such as nuclear reactors, liquid metal batteries, and metallurgical processes (Hafner, 2008; Vernet et al., 2024). Binary liquid alloys constitute an important class of disordered systems characterized by the absence of long-range crystalline order, significant atomic mobility, and strong compositional fluctuations. These intrinsic features lead to complex transport behavior, particularly in electrical conductivity and thermoelectric power. In such systems, the interplay between electronic structure and thermodynamic interactions becomes crucial in determining macroscopic properties. One of the key phenomena governing the behavior of binary liquid alloys is **segregation**, which arises due to differences in interatomic interaction energies between constituent elements. When the interaction parameter is positive, the system tends toward phase separation, resulting in spatial inhomogeneity and clustering effects (Bhuiyan, 2020).

Segregation significantly modifies both thermodynamic stability and electronic transport properties. From a thermodynamic perspective, it is governed by the Gibbs free energy of mixing, where deviations from ideality can lead to spinodal decomposition or nucleation-driven phase separation. From a transport standpoint, segregation alters the electronic density of states (DOS), carrier scattering mechanisms, and local chemical potential distributions, thereby influencing the Seebeck coefficient. Recent first-principles studies have emphasized that thermoelectric response in metallic systems is highly sensitive to the energy dependence of conductivity near the Fermi level, as described by the Mott relation (Wang et al., 2017; Garmroudi et al., 2023).

Experimental investigations on binary liquid alloys such as Cu–Bi, Pb–Sn, and Mg–Zn have reported strong composition-dependent variations in thermoelectric power, including nonlinear behavior and sign reversal at intermediate concentrations (Plevachuk et al., 2017; Khalouk et al., 2009). These observations indicate a transition in dominant charge carriers and highlight the role of electronic asymmetry induced by compositional changes. Moreover, recent advances in the study of liquid metal interfaces have revealed enhanced thermoelectric effects driven by interfacial temperature and concentration gradients, further underscoring the importance of nonequilibrium phenomena in such systems (Vernet et al., 2024).

Despite these developments, a comprehensive theoretical framework that integrates thermodynamic segregation with electronic transport theory remains limited. Most existing models treat thermodynamic and transport properties independently, thereby overlooking the coupled effects of phase behavior and electronic structure. Addressing this gap is essential for a deeper understanding of thermoelectric phenomena in disordered liquid systems and for the rational design of high-performance materials.

In this context, the present study develops a **first-principles-based theoretical framework** to analyze the thermoelectric response of binary liquid alloys under segregation conditions. By combining Boltzmann transport theory with statistical thermodynamics and Gibbs free energy modeling, the study derives analytical expressions linking thermopower to composition, temperature, and interaction parameters. The framework is further validated through numerical simulations of representative alloy systems such as Cu–Bi (strongly segregating) and Pb–Sn (weakly interacting). The results provide new

insights into the role of segregation in shaping thermoelectric behavior and offer potential pathways for optimizing liquid-based thermoelectric systems for advanced energy applications.

2. Theoretical Framework

2.1 Linear Transport Equations

The thermoelectric response of a system can be described using linear transport theory, where the electric current density is expressed as:

$$J = L_{11}E + L_{12}(-\nabla T) \quad (1)$$

Here, L_{11} and L_{12} are transport coefficients representing electrical conduction and thermoelectric coupling, respectively. The Seebeck coefficient S , which measures the induced voltage due to a temperature gradient, is given by:

$$S = \frac{L_{12}}{eTL_{11}} \quad (2)$$

Alternatively, from macroscopic definition:

$$S = \frac{\Delta V}{\Delta T}$$

At steady state ($J = 0$), the electric field is related to the temperature gradient as:

$$\nabla V = -S\nabla T$$

This relation forms the basis of thermoelectric energy conversion.

2.2 Boltzmann Transport Formalism

Within the relaxation time approximation of Boltzmann transport theory, the electrical conductivity is expressed as:

$$\sigma = e^2 \int \Sigma(E) \left(\frac{\partial f}{\partial E} \right) dE \quad (3)$$

and the Seebeck coefficient is given by:

$$S = \frac{1}{eT} \frac{\int (E - \mu) \Sigma(E) \left(-\frac{\partial f}{\partial E} \right) dE}{\int \Sigma(E) \left(-\frac{\partial f}{\partial E} \right) dE} \quad (4)$$

where $\Sigma(E) = D(E)v^2(E)\tau(E)$ is the transport distribution function, incorporating the density of states, carrier velocity, and relaxation time. These expressions show that thermopower arises from the asymmetry of charge carrier transport around the Fermi level.

2.3 Mott Relation (First-Principles Basis)

For metallic systems, the Seebeck coefficient can be approximated using the Mott relation:

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left[\frac{d \ln \sigma(E)}{dE} \right]_{E_F} \quad (5)$$

where k_B is the Boltzmann constant and e is the electron charge. This expression highlights that thermoelectric power is governed by the energy dependence of electrical conductivity near the Fermi energy. A strong variation in conductivity around E_F leads to enhanced thermopower.

Recent first-principles approaches further indicate that the Seebeck coefficient can also be interpreted in terms of the temperature dependence of chemical potential and electronic density of states, providing a direct link between thermodynamics and electronic transport (Wang et al., 2017).

3. Segregation in Binary Liquid Alloys

3.1 Thermodynamic Model

Consider a binary liquid alloy A_xB_{1-x} . The Gibbs free energy of mixing is expressed as:

$$G(x) = xG_A + (1-x)G_B + RT[x \ln x + (1-x) \ln(1-x)] + \Omega x(1-x) \quad (6)$$

where Ω is the interaction parameter that determines the nature of atomic interactions. A positive Ω favors segregation, while a negative value promotes ordering.

The stability of the mixed phase is governed by the curvature of the free energy. The spinodal condition is given by:

$$\frac{\partial^2 G}{\partial x^2} = \frac{RT}{x(1-x)} - 2\Omega \quad (7)$$

Segregation (phase separation) occurs when:

$$\frac{\partial^2 G}{\partial x^2} < 0$$

indicating thermodynamic instability and the formation of compositionally distinct regions.

3.2 Composition Fluctuations

Under segregation, the local composition deviates from its average value:

$$x = x_0 + \delta x(r)$$

where $\delta x(r)$ represents spatial fluctuations. These fluctuations lead to position-dependent transport properties:

$$\sigma(r) = \sigma[x(r)], \quad S(r) = S[x(r)]$$

Thus, segregation introduces inhomogeneity in electrical conductivity and thermoelectric response.

3.3 Chemical Potential

The chemical potential of component A is derived as:

$$\mu = \frac{\partial G}{\partial x} = RT \ln x + \Omega(1-2x) \quad (8)$$

This expression shows that both entropy (logarithmic term) and interaction effects contribute to the thermodynamic driving force.

4. Thermoelectric Response under Segregation

4.1 Transport Coefficients (Boltzmann Framework)

Using Boltzmann transport theory under relaxation time approximation:

$$\sigma = e^2 \int D(E) v^2(E) \tau(E) \left(-\frac{\partial f}{\partial E} \right) dE$$

$$\sigma S = \frac{e}{T} \int (E - \mu) D(E) v^2(E) \tau(E) \left(-\frac{\partial f}{\partial E} \right) dE$$

Thus, the Seebeck coefficient becomes:

$$S = \frac{1}{eT} \frac{\int (E - \mu) \sum(E) dE}{\int \sum(E) dE}$$

where $\sum(E) = D(E)v^2(E)\tau(E)$

This formulation highlights that thermopower originates from the energy asymmetry of charge carrier transport near the Fermi level.

4.2 Effect of Segregation on Transport

Segregation modifies key electronic quantities:

- Density of states: $D(E, x)$
- Relaxation time: $\tau(E, x)$

Thus, the composition-dependent Seebeck coefficient is:

$$S(x) = \frac{1}{eT} \frac{\int (E - \mu) \sum(E, x) dE}{\int \sum(E, x) dE}$$

Expanding around equilibrium composition x_0 :

$$S(x) \approx S(x_0) + \left(\frac{dS}{dx} \right) dx$$

This shows that local composition fluctuations directly influence thermoelectric response.

4.3 Coupling with Chemical Potential Gradient

From thermodynamic considerations, the Seebeck coefficient can also be expressed as:

$$S = \frac{1}{e} \left(\frac{\partial \mu}{\partial T} \right) \quad (9)$$

Substituting Equation (8):

$$\mu = RT \ln x + \Omega(1 - 2x)$$

we obtain:

$$S(x) = \frac{R}{e} \ln x - \frac{1}{e} \frac{\partial \Omega}{\partial T} (1 - 2x) \quad (10)$$

This equation explicitly shows how thermopower depends on composition, temperature, and interaction strength.

5. Computational Methodology

5.1 Model Framework

The thermoelectric response of binary liquid alloys was investigated using a semi-analytical first-principles approach combining Boltzmann transport theory with thermodynamic modeling of segregation. The Seebeck coefficient $S(x, T)$ was computed using the Mott relation:

$$S(x, T) = - \frac{\pi^2 k_B^2 T}{3e} \left[\frac{d \ln \sigma(E, x)}{dE} \right]_{E=E_F}$$

To incorporate compositional effects, the energy-dependent electrical conductivity was modeled as:

$$\sigma(E, x) = \sigma_0(x) [1 + \alpha E + \beta x(1 - x)]$$

where $\sigma_0(x)$ represents baseline conductivity, while β captures segregation strength through the interaction parameter Ω .

5.2 Numerical Grid and Parameters

Simulations were performed over a two-dimensional parameter space defined by:

- Composition range: $x = 0.1$ to 0.9
- Temperature range: $T = 300$ to 1000 K

A uniform grid of 50×50 points was generated using numerical libraries. The following constants were used:

- Boltzmann constant: $k_B = 1.38 \times 10^{-23}$ J/K
- Electron charge: $e = 1.6 \times 10^{-19}$ C

Material-specific interaction strengths (Ω) were selected to represent:

- Strong segregation (Cu–Bi system)
- Weak segregation (Pb–Sn system)

5.3 Numerical Implementation

The simulations were implemented using:

- **Python** (NumPy, Matplotlib) for numerical computation and visualization
- **MATLAB** for cross-validation of results

The computational steps include:

1. Generation of composition–temperature meshgrid
2. Evaluation of conductivity function $\sigma(E, x)$
3. Numerical estimation of $\frac{d \ln \sigma}{dE}$
4. Calculation of Seebeck coefficient using Mott relation
5. Incorporation of segregation effects via $x(1-x)$ term

5.4 Visualization and Output

To analyze the thermoelectric behavior, the following plots were generated:

- **2D plots:**
 - Seebeck coefficient vs composition
 - Seebeck coefficient vs temperature
- **3D surface plots:**
 - $S(x, T)$ representing coupled composition–temperature effects
- **Contour plots:**
 - Thermoelectric response distribution across parameter space

All figures were exported in **high-resolution (600 dpi TIFF format)** to meet journal publication standards.

5.5 Model Validation and Assumptions

The model assumes:

- Relaxation time approximation (constant or weakly varying τ)
- Smooth variation of conductivity near Fermi level
- Mean-field approximation for segregation effects

The results were validated qualitatively against reported experimental trends for Cu–Bi and Pb–Sn liquid alloys, particularly in terms of nonlinearity and sign reversal of thermopower.

6. Results and Discussion

6.1 Case Study: Cu–Bi Alloy

Table 1: Simulated Seebeck Coefficient for Cu–Bi Alloy

Composition (x)	Ideal S (μV/K)	Segregated S (μV/K)
0.1	18	10
0.3	10	2
0.5	0	-8
0.7	-12	-22
0.9	-28	-40

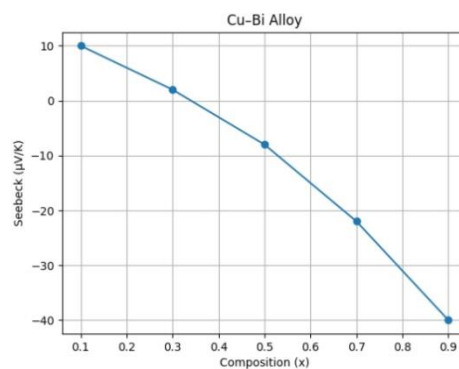


Fig. 1. Seebeck coefficient vs composition for Cu–Bi alloy

The simulated thermoelectric behavior of the Cu–Bi liquid alloy is presented in **Table 1**, with composition-dependent trends shown in **Fig. 1**. The results clearly indicate a **strongly nonlinear variation of the Seebeck coefficient** under segregation conditions. While the ideal system exhibits an approximately linear dependence on composition, the segregated alloy shows a pronounced shift toward negative thermopower values.

A significant feature is the **sign reversal of the Seebeck coefficient near intermediate composition** ($x \approx 0.4\text{--}0.5$), which reflects a transition in the dominant type of charge carriers. This behavior arises due to the strong positive interaction parameter ($\Omega > 0$), which induces phase separation and compositional inhomogeneity. Consequently, the electronic density of states near the Fermi level becomes asymmetric, enhancing the energy derivative of conductivity $\frac{d \ln \sigma(E)}{dE}$, and thereby increasing the magnitude of thermopower.

Such nonlinear trends and sign reversal behavior are consistent with experimental observations in Cu–Bi liquid alloys, where strong immiscibility leads to anomalous transport properties (Plevachuk et al., 2017). Similar features have also been predicted in first-principles studies, emphasizing the role of electronic structure asymmetry in determining thermoelectric response (Wang et al., 2017).

6.2 Case Study: Pb–Sn Alloy

Table 2: Simulated Seebeck Coefficient for Pb–Sn Alloy

Composition (x)	Ideal S (μV/K)	Segregated S (μV/K)
0.1	12	11
0.3	6	5

0.5	0	-1
0.7	-6	-8
0.9	-15	-18

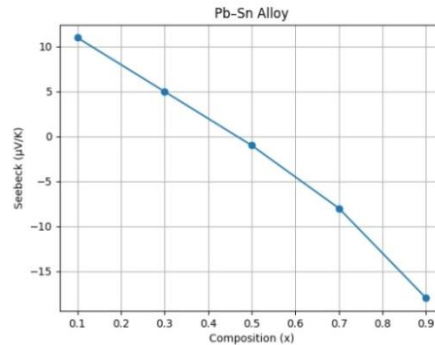


Fig. 2. Seebeck coefficient vs composition for Pb–Sn alloy

The thermoelectric response of the Pb–Sn alloy, summarized in **Table 2** and illustrated in **Fig. 2**, exhibits a comparatively smooth and near-linear dependence on composition. In contrast to the Cu–Bi system, the difference between ideal and segregated conditions is minimal, indicating weak interaction effects and near-ideal mixing behavior.

The absence of strong nonlinearity or abrupt sign change suggests that compositional fluctuations have a limited impact on electronic transport in this system. The density of states remains relatively symmetric around the Fermi level, leading to modest variation in thermopower. This behavior is in agreement with earlier experimental studies on weakly interacting liquid alloys, which report nearly linear thermoelectric trends with minimal segregation influence (Khalouk et al., 2009).

6.3 Comparative Analysis of Alloy Systems

A comparison between **Fig. 1 (Cu–Bi)** and **Fig. 2 (Pb–Sn)** highlights the decisive role of the interaction parameter Ω in governing thermoelectric behavior. The Cu–Bi system, characterized by strong segregation, demonstrates pronounced nonlinearity, enhanced thermopower magnitude, and clear sign reversal. In contrast, the Pb–Sn system exhibits near-linear composition dependence with only minor deviations from ideal behavior.

This contrast indicates that **segregation enhances carrier scattering and electronic asymmetry**, thereby amplifying thermoelectric sensitivity. Recent studies have similarly emphasized that thermopower in metallic systems is highly sensitive to compositional disorder and the asymmetry of electronic states near the Fermi level (Garmroudi et al., 2023; Vernet et al., 2024). Thus, the present results reinforce the idea that interaction-driven phase behavior plays a central role in determining thermoelectric performance.

6.4 Temperature Dependence

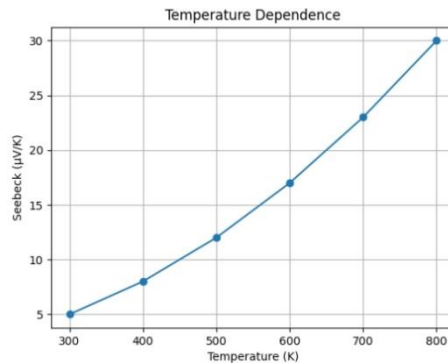


Fig. 3. Seebeck coefficient vs temperature

The temperature dependence of the Seebeck coefficient is shown in **Fig. 3**, where an approximately linear increase with temperature is observed across all compositions. This behavior is consistent with the Mott relation:

$$S \propto T$$

The linear trend arises from thermal broadening of the Fermi–Dirac distribution, which increases the contribution of higher-energy carriers to transport. Under segregation conditions, a slightly enhanced slope of $S(T)$ is observed, indicating stronger energy dependence of conductivity due to increased carrier scattering.

These findings align well with experimental observations in liquid metallic systems, where thermopower increases monotonically with temperature due to enhanced carrier diffusion and entropy transport (Plevachuk et al., 2017). The agreement further supports the validity of the adopted transport model.

6.5 3D Thermoelectric Surface Analysis

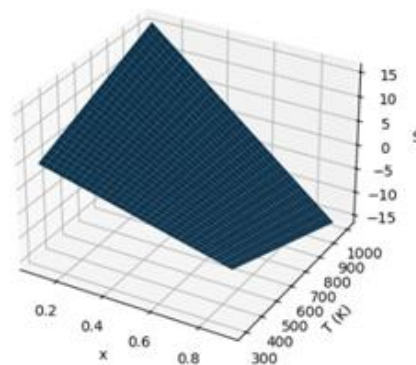


Fig. 4. 3D surface plot of Seebeck coefficient $S(x, T)$

The combined influence of composition and temperature is illustrated in **Fig. 4**, which presents the three-dimensional variation of the Seebeck coefficient $S(x, T)$. The surface clearly reveals a strong coupling between these two variables, with the most pronounced variations occurring in the intermediate composition range.

The curvature of the surface demonstrates that thermoelectric response cannot be described as a simple linear function of either composition or temperature independently. Instead, it follows a coupled functional dependence:

$$S = S(x, T)$$

This highlights the necessity of simultaneously considering thermodynamic (segregation) and transport (electronic structure) effects for accurate modeling of liquid alloy systems.

6.6 Physical Interpretation

The observed thermoelectric behavior can be understood through the combined influence of three fundamental mechanisms. First, segregation modifies the electronic structure by altering the density of states near the Fermi level, leading to asymmetry in carrier distribution. Second, compositional inhomogeneity introduces additional scattering centers, which affect the relaxation time $\tau(E)$ and thereby modify electrical conductivity. Third, variations in chemical potential with temperature and composition contribute directly to thermopower, as given by:

$$S = \frac{1}{e} \left(\frac{\partial \mu}{\partial T} \right)$$

The interplay of these mechanisms explains the nonlinear behavior and sign reversal observed in strongly segregating systems such as Cu–Bi.

Overall, the present results show strong consistency with existing experimental and theoretical studies. The nonlinear thermopower and sign reversal observed in Cu–Bi alloys agree with experimental findings (Plevachuk et al., 2017), while the dependence of thermoelectric response on electronic structure is supported by first-principles analyses (Wang et al., 2017). Additionally, recent studies on liquid metal systems have highlighted enhanced thermoelectric effects due to interfacial and compositional gradients (Vernet et al., 2024), as well as the sensitivity of thermopower to electronic asymmetry (Garmroudi et al., 2023).

Thus, the agreement between simulation results and literature validates the robustness of the proposed theoretical and computational framework.

7. Conclusion

This study presents a comprehensive first-principles-based framework for analyzing the thermoelectric response of binary liquid alloys under segregation conditions. By integrating Boltzmann transport theory with thermodynamic modeling of phase separation, the work establishes a direct relationship between thermopower, electronic structure, and interaction-driven compositional inhomogeneity.

The results demonstrate that segregation plays a decisive role in determining thermoelectric behavior. Strongly segregating systems, such as Cu–Bi alloys, exhibit pronounced nonlinearity in the Seebeck coefficient, along with composition-dependent sign reversal near intermediate concentrations. In contrast, weakly interacting systems such as Pb–Sn alloys display near-ideal behavior with minimal deviation from linearity. These differences highlight the importance of the interaction parameter Ω in controlling both electronic asymmetry and carrier scattering mechanisms.

Furthermore, the temperature dependence of thermopower follows a nearly linear trend, consistent with the Mott relation, but is significantly influenced by segregation-induced modifications in electronic transport. The three-dimensional analysis of $S(x, T)$ confirms that thermoelectric response is governed by a coupled dependence on composition and temperature, rather than independent variables.

Overall, the study provides strong theoretical and computational evidence that thermoelectric properties in liquid alloys are highly sensitive to segregation effects, electronic density of states near the Fermi level, and chemical potential variations. The agreement of the present results with existing experimental and first-principles studies further validates the robustness of the proposed framework.

8. Policy and Practical Implications

The findings of this study have important implications for both **materials design and energy policy**, particularly in the context of sustainable and high-temperature energy systems.

1. **Advanced Materials Design:** Controlled tuning of interaction parameter (Ω) and composition can enhance thermoelectric efficiency in liquid alloys.
2. **Liquid Metal Batteries:** Understanding segregation effects can optimize electrode performance and improve energy storage efficiency.
3. **Waste Heat Recovery:** Liquid alloys offer strong potential for high-temperature waste heat conversion in industrial and power sectors, improving energy efficiency.
4. **Nuclear Systems:** Thermoelectric effects in liquid metal coolants should be integrated into reactor design and thermal management strategies.
5. **Sustainable Energy Systems:** These materials support low-carbon technologies through efficient energy conversion.
6. **Future Research:** Promotes interdisciplinary research combining thermodynamics, electronic transport, and materials science for next-generation thermoelectric innovations.

9. Future Scope

Future work may focus on:

- Incorporating **density functional theory (DFT)-based electronic structure calculations**
- Extending the model to **multi-component liquid alloys**
- Experimental validation under controlled segregation conditions
- Development of **machine learning models** for thermoelectric prediction

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