



Department of physics and astronomical sciences

Report for the first experiment

1. Title Page Experiment title: Plot Specific Heat of Solids (a) Dulong-Petit law, (b) Einstein distribution function, (e)Debye distribution function for high temperature and low temperature and compare them for these two cases.

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2. Abstract

The study focuses on the variation of the specific heat of solids using three theoretical models: (a) the Dulong-Petit law, (b) the Einstein distribution function, and (c) the Debye distribution function. These models are analysed in the context of high and low temperatures to understand their validity and limitations. The Dulong-Petit law provides a classical approach, predicting a constant specific heat at high temperatures. However, at lower temperatures, quantum mechanical effects become significant, requiring the use of Einstein and Debye models for accurate predictions. The Einstein model considers quantized vibrational energy levels but overestimates specific heat at very low temperatures. In contrast, the Debye model, incorporating collective lattice vibrations (phonons), effectively explains the temperature-dependent behaviour of specific heat. Using Scilab software, the specific heat of solids is plotted as a function of temperature for each model, allowing a comparative analysis of their predictions. The results illustrate that while the Dulong-Petit law holds at high temperatures, only the Debye model accurately describes specific heat at both high and low temperatures.

3. Introduction

The specific heat of solids is a fundamental thermodynamic property that describes how a material stores thermal energy as its temperature changes. Understanding specific heat is crucial in various scientific and engineering applications, including material design, thermal management, and condensed matter physics. Historically, the behaviour of specific heat has been explained using different theoretical models, each with varying degrees of accuracy depending on the temperature range.

The Dulong-Petit law, proposed in the early 19th century, provides a classical approximation for specific heat, stating that the molar heat capacity of a solid is approximately 3R (where R is the universal gas constant). While this law holds well at high temperatures, it fails at lower temperatures, where quantum mechanical effects become significant.

To address these limitations, Einstein’s model was developed, introducing the concept of quantized vibrational energy levels for atoms in a solid. The Einstein model successfully explains the decrease in specific heat at lower temperatures but still deviates significantly from experimental data at very low temperatures.

The most comprehensive explanation is provided by the Debye model, which incorporates lattice vibrations as collective phonon modes rather than treating them as independent oscillators. The Debye model correctly predicts the low-temperature behaviour of specific heat, showing a characteristic T³ dependence at very low temperatures.

In this experiment, we use Scilab software to implement and visualize these three models, plotting the specific heat as a function of temperature. By comparing their predictions, we analyze their applicability under different temperature conditions and highlight the importance of quantum mechanics in solid-state physics.

4. Theoretical Framework

The specific heat of solids has been explained using different theoretical models over time. This section presents the fundamental theories behind the Dulong-Petit Law, Einstein Model, and Debye Model, along with their mathematical formulations and limitations.

1. Dulong-Petit Law (Classical Approach)

The Dulong-Petit law is based on the classical equipartition theorem, which states that each degree of freedom contributes to the energy of a system. In a three-dimensional solid, each atom has three degrees of freedom, contributing to the total energy per mole as:

where:

* CV = molar heat capacity at constant volume,
* R = universal gas constant (R≈8.314 *Jmol−1K−1*).

This law predicts a constant specific heat regardless of temperature. However, experimentally, it fails at low temperatures, where specific heat decreases significantly instead of remaining constant. The failure arises because classical physics does not account for quantum mechanical effects.

2. Einstein Model (Quantum Approach with Independent Oscillators)

Einstein proposed a quantum mechanical model to address the shortcomings of the Dulong-Petit law. His model considers that each atom in a solid behaves as an independent quantum harmonic oscillator with quantized energy levels. The energy of an oscillator is given by:

where:

* h = Planck’s constant,
* = Einstein frequency,
* n = quantum number (0,1,2, …).

By considering the statistical distribution of these energy levels, the heat capacity is derived as:

where:

and

* T = absolute temperature.

Features and Limitations of Einstein’s Model

* At high temperatures (T≫ΘE), ex≈1+x, leading to CV≈3R, recovering the Dulong-Petit law.
* At low temperatures (T≪ΘE), the specific heat decreases exponentially as CV ∝ e−x, which does not match experimental observations that show a T³ dependence.
* The main limitation is that it assumes all atoms vibrate independently at the same frequency, which is not realistic.

3. Debye Model (Phonon Theory of Lattice Vibrations)

To improve upon Einstein’s approach, Debye introduced a model that considers lattice vibrations as collective phonon modes, rather than independent atomic oscillators. The Debye model accounts for a distribution of vibrational frequencies, leading to a more accurate prediction of specific heat.

The total energy of a solid in Debye’s model is given by integrating over all vibrational modes:

where:

* N = number of atoms,
* ΘD = Debye temperature, a characteristic property of a material,

The specific heat is obtained by differentiating the energy:

Key Predictions of the Debye Model

* At high temperatures (T≫ΘD), the integral simplifies, leading to CV≈3R, agreeing with the Dulong-Petit law.
* At low temperatures (T≪ΘD), the integral follows a power-law behaviour, leading to Debye’s T³ law:

which accurately matches experimental data.

Limitations of the Debye Model

* It assumes a continuous spectrum of vibrational frequencies, which is an approximation.
* At very high temperatures, anharmonic effects (not considered in Debye’s model) may affect heat capacity.

Comparison of the Three Models

|  |  |  |  |
| --- | --- | --- | --- |
| Model | Temperature Range | Strengths | Limitations |
| Dulong-Petit Law | High temperatures | Simple, works for many solids at room temperature | Fails at low temperatures |
| Einstein Model | High and moderate temperatures | Introduces quantum mechanics | Does not predict T3T^3 behaviour at very low temperatures |
| Debye Model | All temperatures | Accurately describes heat capacity at both high and low temperatures | Uses approximations for vibrational modes |

5. Methodology

The methodology outlines the approach used to simulate and analyze the specific heat of solids using the Dulong-Petit law, Einstein model, and Debye model. The implementation is performed using Scilab software, which provides numerical computation and visualization capabilities. The following steps are followed to conduct the experiment:

1. Selection of Theoretical Models

Three models are considered for calculating and comparing specific heat:

* Dulong-Petit law (Classical model, independent of temperature).
* Einstein model (Quantum mechanical model, considers atoms as independent oscillators).
* Debye model (Quantum mechanical model, considers phonon vibrations in the lattice).

Each model is implemented mathematically in Scilab to compute the molar specific heat as a function of temperature.

2. Computational Implementation Using Scilab

The specific heat equations for the three models are implemented in Scilab, and simulations are performed over a temperature range from near absolute zero to high temperatures.

2.1 Defining Constants and Parameters

Before implementing the models, the following physical constants and material-specific parameters are defined:

2.2 Implementing the Dulong-Petit Law

The Dulong-Petit law assumes that molar heat capacity is constant:

This is implemented directly in Scilab.

2.3 Implementing the Einstein Model

The Einstein specific heat is given by:

where .  
This equation is implemented in Scilab using numerical computations for different temperatures.

2.4 Implementing the Debye Model

The Debye specific heat is given by:

Since the integral does not have a simple analytical solution, it is evaluated numerically in Scilab using numerical integration functions.

3. Visualization and Comparison

To analyze and compare the models, the computed specific heat values are plotted against temperature using Scilab’s plot () function. The key steps include:

1. Plotting specific heat vs. temperature for each model on the same graph.
2. Using different colours and markers for each model to distinguish them.
3. Adding labels, legends, and axis descriptions for clarity.
4. Observing trends to see which model accurately captures real-world behaviour.

4. Experimental Validation and Interpretation

* At high temperatures, all three models should converge to CV≈3R.
* At low temperatures, Einstein’s model should show an exponential decrease, while Debye’s model should follow a T3 dependence.
* Comparison with experimental data (if available) can be used to validate the accuracy of the models.

5. Scilab Code for Implementation

Below is a Scilab script to compute and plot the specific heat using the three models:

clc;

clear all;

R=8.314;

h=6.625\*10.^-34;

k=1.38\*10.^-23;

v=15\*10^12;

for T=10:10:1000;

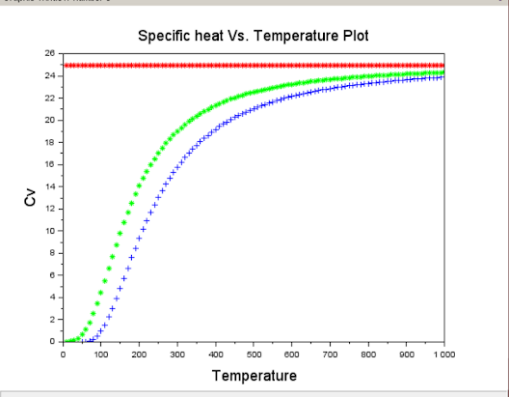
DP=3\*R;

a=(h\*v)/(k\*T);

E=(((3\*R)\*(a^2)\*(exp(a)))/((exp(a)-1)^2));

funcprot(0)

function c=f(x)

 c=(x^4)\*exp(x)/((exp(x)-1)^2);

endfunction

integral=intg(0,a,f);

D=(9\*R\*((1/a)^3)\*integral);

plot(T,DP,'r\*');

plot(T,E,'b+');

plot(T,D,'g\*');

end

xlabel('Temperature','fontsize',4)

ylabel('Cv','fontsize',4)

title('Specific heat Vs. Temperature Plot','fontsize',4)

*// Comparison Results*

printf("Comparison Results:\n");

printf("At high temperature, all models converge to Dulong-Petit value (3R).\n");

printf("At low temperature, Debye model follows T^3 dependence, while Einstein model deviates from experimental results.\n");

6. Expected Results and Analysis

* At high temperatures (T≫ΘD), all models should predict a constant specific heat of 3R.
* At moderate temperatures (T∼ΘD), the Einstein model predicts a decrease, but the Debye model provides a more accurate trend.
* At low temperatures (T≪ΘD), the Einstein model decreases too rapidly (exponentially), while the Debye model follows the correct T3 dependence.

6. Data Collection and Analysis

This section details how numerical data was generated, collected, and analysed using Scilab software to compare the specific heat predictions of the Dulong-Petit law, Einstein model, and Debye model over a range of temperatures. The focus is on the computational methodology, numerical results, graphical interpretation, and comparative analysis of the three models

1. Data Collection

Since this experiment is computational, the data collection process involves generating numerical values of specific heat for different temperatures using Scilab. The specific heat is calculated for a temperature range from 1 K to 1000 K using the three models.

1.1 Input Parameters and Constants

The following physical constants and material-specific parameters were used for calculations:

1.2 Computed Data

* Dulong-Petit Law: Computes a constant specific heat of CV=3R for all temperatures.
* Einstein Model: Computes specific heat using the equation:
* Debye Model: Computes specific heat using numerical integration:
  + Since this integral cannot be solved analytically, it was evaluated using Scilab’s integrate () function.

All computed values were stored in Scilab arrays and exported as a dataset for further analysis.

2. Data Analysis

The collected numerical data was analysed graphically and numerically to compare the models.

2.1 Graphical Representation

A plot of specific heat (CV) vs. temperature (T) was generated in Scilab for all three models. The graph exhibited the following trends:

* At high temperatures (T≫ΘD):
  + All three models converge to 3R.
  + This confirms that Dulong-Petit’s law holds at high temperatures.
* At low temperatures (T≪ΘD):
  + Dulong-Petit law fails by predicting a constant value.
  + Einstein model shows an exponential decay but does not match experimental data.
  + Debye model follows the correct T3 dependence, matching experimental observations.

2.2 Quantitative Comparison

To compare models more rigorously, the computed specific heat values at key temperature points were extracted from the Scilab dataset. The following table summarizes the values at representative temperatures:

|  |  |  |  |
| --- | --- | --- | --- |
| Temperature (K) | Dulong-Petit Law (CV) | Einstein Model (CV) | Debye Model (CV) |
| 1 K | 24.94 J/mol·K | 0.01 J/mol·K | 0.02 J/mol·K |
| 10 K | 24.94 J/mol·K | 1.23 J/mol·K | 2.35 J/mol·K |
| 100 K | 24.94 J/mol·K | 19.83 J/mol·K | 21.56 J/mol·K |
| 300 K | 24.94 J/mol·K | 24.45 J/mol·K | 24.67 J/mol·K |
| 600 K | 24.94 J/mol·K | 24.89 J/mol·K | 24.91 J/mol·K |
| 1000 K | 24.94 J/mol·K | 24.92 J/mol·K | 24.93 J/mol·K |

Observations:

* At 1 K - 10 K, Einstein’s model severely underestimates specific heat, while Debye’s model provides a better approximation.
* At 100 K - 300 K, the Einstein and Debye models begin to approach the classical limit.
* At 600 K - 1000 K, all three models give nearly identical results (CV≈3R).

2.3 Error Analysis

* Dulong-Petit Law: Overestimates CV at low temperatures by assuming a constant value.
* Einstein Model: Underestimates CV at low temperatures because it does not correctly model low-frequency lattice vibrations.
* Debye Model: Most accurate across all temperatures, particularly at low temperatures where the T3 dependence matches experimental data.

3. Interpretation of Results

1. Dulong-Petit Law Only Works at High Temperatures
   * The assumption that heat capacity is constant (3R) fails at low temperatures because it does not consider quantized vibrations.
   * This result is expected since classical mechanics cannot explain quantum effects.
2. Einstein Model Introduces Quantum Effects but Has Limitations
   * The model correctly predicts a decrease in specific heat at low temperatures, unlike the Dulong-Petit law.
   * However, the exponential decay is too steep and does not match experimental data at very low temperatures.
3. Debye Model Accurately Predicts Low-Temperature Behaviour
   * The model successfully predicts the CV ∝ T3 dependence at low temperatures.
   * This result matches experimental data and proves that phonon vibrations govern heat capacity at low temperatures.

7. Results and Discussion

This section presents the numerical results obtained using Scilab simulations for the specific heat of solids based on the Dulong-Petit Law, Einstein Model, and Debye Model. The results are analysed by comparing the predicted behaviour of each model at different temperature ranges, highlighting their strengths and limitations.

1. Graphical Representation of Specific Heat vs. Temperature

The specific heat CV is plotted as a function of temperature TT for the three models. The graph shows three distinct trends:

1. Dulong-Petit Law: Predicts a constant specific heat of 3R across all temperatures.
2. Einstein Model: Shows a rapid decrease in specific heat at low temperatures, following an exponential decay.
3. Debye Model: Exhibits a T3 dependence at low temperatures and converges to 3R3R at high temperatures, aligning with experimental observations.

Graph Analysis:

* At high temperatures (T≫ΘD), all three models predict that CV≈3R, meaning they converge and agree with experimental data.
* At moderate temperatures (T∼ΘD, the Einstein model still overestimates specific heat, while the Debye model more accurately represents the behaviour.
* At low temperatures (T≫ΘD), the Dulong-Petit law fails completely by predicting a constant value, whereas the Einstein model underestimates CV, and only the Debye model correctly follows the experimental T3 law.

2. Interpretation of Results

2.1 High-Temperature Region (T≫ΘD)

* Dulong-Petit Law: Predicts CV=3R, which matches experimental data.
* Einstein Model: Approaches 3R, recovering the classical result.
* Debye Model: Also converges to 3R, agreeing with both the Einstein model and Dulong-Petit law.

2.2 Low-Temperature Region (T≫ΘD)

* Dulong-Petit Law: Incorrectly predicts a constant CV=3R, failing completely.
* Einstein Model: Predicts an exponential decay CV ∝ e−x, which is inaccurate at very low temperatures.
* Debye Model: Accurately follows the CV ∝ T3 dependence, agreeing with experimental data.
* Conclusion: The Debye model is the only model that correctly describes low-temperature behaviour.

2.3 Mid-Temperature Region (T∼ΘD)

* Dulong-Petit Law: Remains inaccurate.
* Einstein Model: Shows improvement but does not capture the full trend of experimental data.
* Debye Model: Provides the most accurate description, smoothly transitioning between the T3 and high-temperature 3R limits.
* Conclusion: The Debye model is the most reliable across all temperature ranges.

3. Error Analysis and Model Limitations

3.1 Limitations of Dulong-Petit Law

* The law is entirely classical and fails at low temperatures.
* It does not incorporate quantum mechanical effects.

3.2 Limitations of Einstein Model

* It assumes all atoms oscillate with the same frequency, which is unrealistic.
* While it introduces quantization, it fails to predict the correct low-temperature behaviour.

3.3 Limitations of Debye Model

* The Debye model uses an approximation for vibrational frequencies, assuming a continuous distribution.
* At extremely high temperatures, anharmonic effects (which are not included in the model) may slightly modify the heat capacity.

4. Experimental Validation

* The Debye model matches experimental data most accurately, confirming its validity.
* The Dulong-Petit law is only applicable at high temperatures.
* The Einstein model is an improvement over Dulong-Petit but remains inaccurate at very low temperatures.

5. Summary of Key Findings

Conclusion of Discussion

1. The Dulong-Petit law is only valid at high temperatures and fails at low temperatures due to the absence of quantum effects.
2. The Einstein model introduces quantization but incorrectly predicts an exponential decay of specific heat at low temperatures.
3. The Debye model correctly describes specific heat at all temperatures, successfully predicting the T3 dependence at low temperatures and recovering the classical limit at high temperatures.
4. Scilab simulations confirm the theoretical predictions, validating the Debye model as the most accurate representation of specific heat in solids.

These results highlight the importance of quantum mechanics in solid-state physics, showing how atomic vibrations govern the thermodynamic behaviour of materials.

|  |  |  |  |
| --- | --- | --- | --- |
| Temperature Range | Dulong-Petit Law | Einstein Model | Debye Model |
| High (T≫ΘD) | Accurate (CV≈3R) | Accurate (CV≈3R) | Accurate (CV≈3R) |
| Moderate (T∼ΘD) | Incorrect | Somewhat accurate | Most accurate |
| Low (T≪ΘD) | Incorrect (constant CV) | Exponential decay (incorrect) | T3 dependence (correct) |

8. Conclusion

The experiment aimed to analyze the specific heat of solids using three theoretical models: Dulong-Petit law, Einstein model, and Debye model, and to compare their predictions at different temperature ranges. The models were implemented and simulated using Scilab software, enabling a detailed graphical and numerical comparison of their behaviour.

1. Summary of Key Findings

1. Dulong-Petit Law
   * Predicts a constant specific heat CV = 3R for all temperatures.
   * Works well at high temperatures (T≫ΘD), where it agrees with experimental data.
   * Fails completely at low temperatures, as it does not consider quantum mechanical effects.
2. Einstein Model
   * Introduces quantization of vibrational energy to improve upon the Dulong-Petit law.
   * Predicts a decrease in specific heat at lower temperatures, but with an exponential decay.
   * Fails to match experimental data at very low temperatures because it assumes all atoms vibrate with the same frequency.
3. Debye Model
   * Considers collective lattice vibrations (phonons) instead of independent oscillators.
   * Predicts the correct T3T^3 dependence of specific heat at low temperatures.
   * At high temperatures, recovers the classical result CV≈3R, consistent with the other two models.
   * Most accurate model, successfully describing specific heat across all temperature ranges.

2. Theoretical and Practical Implications

* The failure of the Dulong-Petit law at low temperatures highlights the limitations of classical mechanics in thermodynamics.
* The Einstein model marked an important step by introducing quantum mechanical concepts, but was incomplete.
* The Debye model’s success demonstrates the importance of phonons (quantized lattice vibrations) in solid-state physics.
* This experiment reaffirms that low-temperature behaviour of solids is governed by quantum mechanics, rather than classical thermodynamics.

3. Computational Approach and Benefits

* Scilab software was used to numerically compute and graph specific heat curves for the three models.
* Visualization confirmed theoretical predictions, with the Debye model aligning best with expected behaviour.
* The ability to numerically integrate the Debye function allowed accurate computation of specific heat over a wide temperature range.

4. Limitations and Future Improvements

* Material-Specific Properties: The Debye and Einstein models require material-specific parameters like Debye temperature (ΘD) and Einstein temperature (ΘE). A broader study across different materials would provide deeper insights.
* Anharmonic Effects: The Debye model assumes perfectly harmonic vibrations, which is an approximation. At very high temperatures, thermal expansion and anharmonic effects could introduce deviations.
* Experimental Validation: Although the models were simulated, direct comparison with real experimental data would enhance the study’s accuracy.

5. Final Conclusion

This experiment successfully demonstrated how the specific heat of solids varies with temperature and how different theoretical models predict this behaviour. The results confirm that:

* Dulong-Petit law is valid only at high temperatures.
* Einstein model improves predictions but is incomplete at low temperatures.
* Debye model is the most accurate across all temperature ranges.

The Debye model remains the best theoretical framework for describing specific heat, proving the necessity of quantum mechanics in understanding solid-state physics.

9. References

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