PHYS 617 - Statistical Mechanics

A Modern Course in Statistical Physics by *Linda E. Reichl*

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Homework 7

Problem 1

(a) Write a computer program to compute the equation of state of a **relativistic** monatomic ideal gas. In practice, you can just make a plot of the energy E as a function of temperature for the gas.

Do this by computing the partition function $Z(\beta)$ by explicit numerical integral, and then taking the derivative of $\ln(Z)$ numerically (by sampling its value at neighboring points and measuring the slope). Show that you get the non-relativistic and ultra-relativistic limits correct and that it transitions at the right temperature.

(b) Take a derivative of $E(T)$ with respect to temperature to get the heat capacity (at constant volume) as a function of temperature. Plot the molar heat capacity as a function of temperature. **Make sure both of the regimes along with the transition point are clearly visible in your plots of $E(T)$ and $C_V(T)$.**

Solution. (a) The energy of a relativistic particle is given by

$$\epsilon^2 = p^2c^2 + m^2c^4 \implies \epsilon = c\sqrt{p^2 + (mc)^2}.$$

The partition function Z is then given by

$$\begin{aligned}
Z &= \sum_{\text{states}} \mathrm{e}^{-\beta\epsilon_q} \\
&= \frac{1}{h^3}\int \mathrm{e}^{-\beta\epsilon_q}\,\mathrm{d}^3x\,\mathrm{d}^3p \\
&= \frac{1}{h^3}\int \mathrm{e}^{-\beta c\sqrt{p^2+(mc)^2}}\,\mathrm{d}^3x\,\mathrm{d}^3p \\
&= \frac{L^3}{h^3}\int \mathrm{e}^{-\beta c\sqrt{p^2+(mc)^2}}\,\mathrm{d}^3p \\
&= \frac{4\pi L^3}{h^3}\int p^2\mathrm{e}^{-\beta c\sqrt{p^2+(mc)^2}}\,\mathrm{d}p.
\end{aligned}$$

We will now integrate this numerically since this is a tough integral to calculate in a closed form (even for symbolic calculators). We will use the function `quad` from the module `scipy.integrate` to integrate what we need and we will vary the temperature T from $0\,\mathrm{K}$ to $5\,\mathrm{K}$. Additionally, we will use units where $c = h = k_B = m_p = 1$. Finally, we will assume a box of length $L = 1\,\mathrm{m}$.

(b) To get the heat capacity (at fixed volume), we just take the derivative of the energy $E(T)$ with respect to the temperature T. We expect the transition point from non-relativistic to ultra-relativistic to be at the temperature T when $k_BT = mc^2 \implies T = 1\,\mathrm{K}$.

```python
import numpy as np
import scipy.integrate as int
import matplotlib.pyplot as plt

############### CONSTANTS ###############
h = 1           # Planck's constant (GeV/Hz)
c = 1           # Speed of light (in natural units)
k_B = 1         # Boltzmann constant (GeV/K)
m_p = 1         # Proton mass (GeV/c^2)
L = 1           # Length of our cube (m)

################## PROBLEM 1 ##################
# TEMPERATURE => 1 K -> 5 K
T = np.linspace(0, 5, 1000)
beta = 1 / (k_B * T)

# INTEGRAL OF PARTITION FUNCTION
def relativisticPartitionFunction(b):
    integrand = int.quad(
        lambda p: p**2 * (np.exp(- b * c * np.sqrt(p**2 + (m_p*c)**2))), 0, np.inf
        )[0]
    return (4*np.pi*L**3)/h**3 * integrand

Z = []
for b in beta:
    z = relativisticPartitionFunction(b)
    Z.append(z)

E = - np.diff(np.log(Z)) / np.diff(beta)

plt.plot(T[:-1], E, 'r', label='Relativistic')
plt.plot(T, (3*k_B*T)/2, 'g', label='Non-Relativistic')
plt.plot(T, 3*k_B*T, 'b', label='Ultra-Relativistic')
# plt.plot(T[:-1], E_discrete, 'k', label='Discrete')
plt.legend(['Relativistic', 'Non-Relativistic', 'Ultra-Relativistic', 'Discrete'])
plt.xlabel('Temperature (K)')
plt.ylabel('Energy')
plt.title('Equation of State of Relativistic Monatomic Ideal Gas')
plt.show()


C_V = np.diff(E) / np.diff(T[:-1])

plt.plot(T[:-2], C_V, 'r', label='Relativistic')
plt.plot(T[:-2], 1.5*np.ones(len(C_V)), 'g', label='Non-Relativistic')
plt.plot(T[:-2], 3*np.ones(len(C_V)), 'b', label='Ultra-Relativistic')
plt.legend(['Relativistic', 'Non-Relativistic', 'Ultra-Relativistic', 'Discrete'])
plt.xlabel('Temperature (K)')
plt.ylabel('Molar Heat Capacity')
plt.title('Molar Heat Capacity of Relativistic Monatomic Ideal Gas')
plt.show()
```

Listing 1: Code for Problem 1

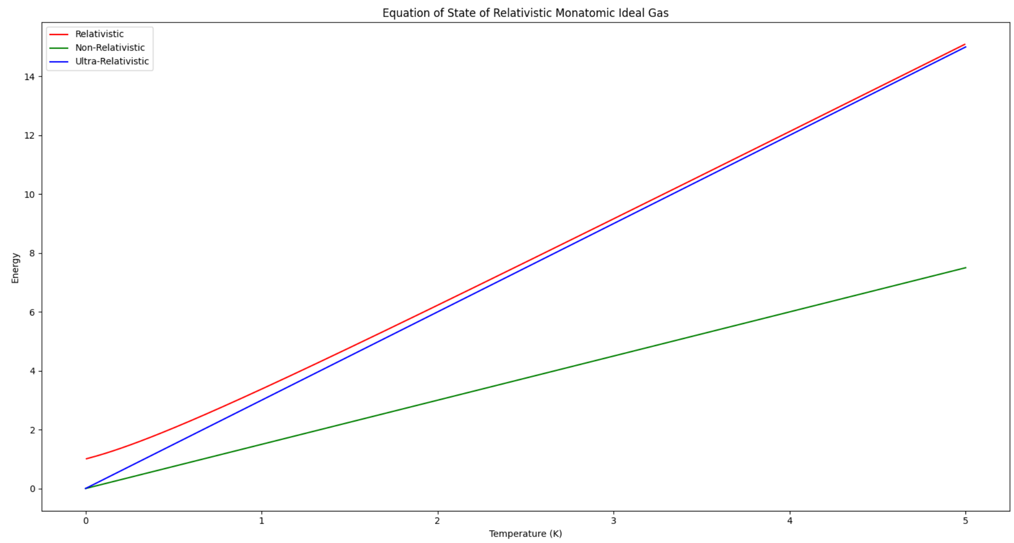

Figure 1: Plot of the energy E as a function of temperature T for the relativistic monatomic ideal gas.

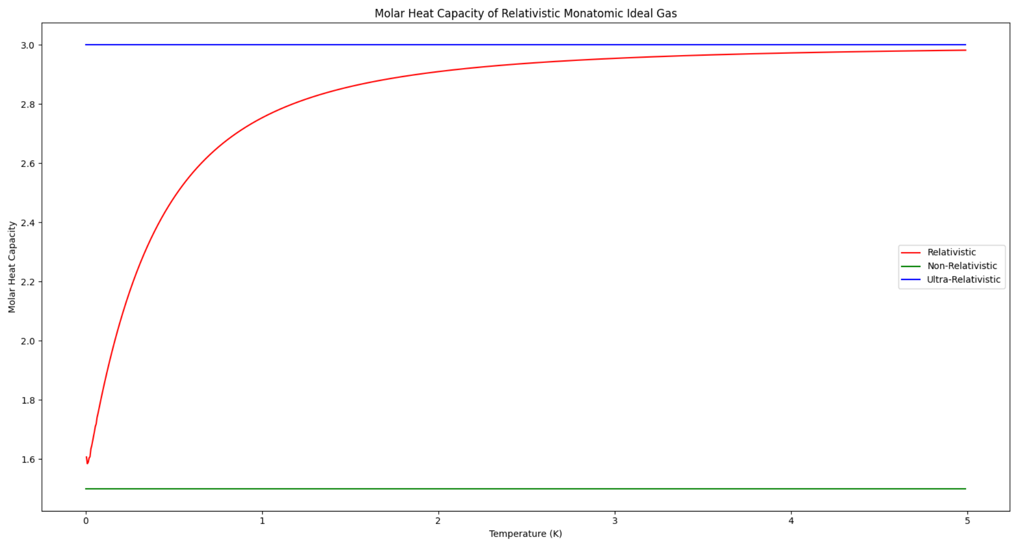

Figure 2: Plot of the molar heat capacity C_V as a function of temperature T for the relativistic monatomic ideal gas.

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Problem 2
Write a computer program to compute the equation of state of a non-relativistic diatomic ideal gas. Again, just make a plot of $E(T)$. Treat the linear momentum integral classically, but include a full computation of the angular momentum term in quantum mechanics:

$$E(p,j) = \frac{p^2}{2m} + \frac{\hbar^2}{2I} j(j+1)$$

(the last term just being the eigenvalue of J^2). When performing the sum over quantum states, remember that there are $2j+1$ possible m eigenstates for every value of j, so the sum looks like:

$$Z = \int \frac{\mathrm{d}^3x\,\mathrm{d}^3p}{h^3} \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \mathrm{e}^{-\beta E(p,j)}$$

Once you have $E(T)$, once again compute the heat capacity $C_V(T)$ (again using numerical derivative). Check behavior at low and high temperatures.

Solution. The energy of a non-relativistic diatomic particle is given by

$$E(p,j) = \frac{p^2}{2m} + \frac{\hbar^2}{2I} j(j+1).$$

The partition function Z is then given by

$$Z = \frac{1}{h^3} \int \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \mathrm{e}^{-\beta E(p,j)}\,\mathrm{d}^3x\,\mathrm{d}^3p.$$

As mentioned in the problem statement, there are $2j+1$ possible m eigenstates for every j. Thus, all different m are $(2j+1)$-degenerate. This gives us

$$\begin{aligned}
Z &= \frac{1}{h^3} \int \sum_{j=0}^{\infty} (2j+1) \mathrm{e}^{-\beta E(p,j)}\,\mathrm{d}^3x\,\mathrm{d}^3p \\
&= \frac{V}{h^3} \int \sum_{j=0}^{\infty} (2j+1) \mathrm{e}^{-\beta\left(\frac{p^2}{2m} + \frac{\hbar^2}{2I} j(j+1)\right)}\,\mathrm{d}^3p \\
&= \frac{V}{h^3} \sum_{j=0}^{\infty} (2j+1) \mathrm{e}^{-\beta \frac{\hbar^2}{2I} j(j+1)} \int \mathrm{e}^{-\beta \frac{p^2}{2m}}\,\mathrm{d}^3p \\
&= \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \sum_{j=0}^{\infty} (2j+1) \mathrm{e}^{-\beta \frac{\hbar^2}{2I} j(j+1)}.
\end{aligned}$$

We find $E(T)$ and $C_V(T)$ in a similar fashion to Problem 1.

```python
############### PROBLEM 2 ###############
T = np.linspace(0.02, 5, 1000)
beta = 1 / (k_B * T)

m_1 = m_p
m_2 = m_p
mu = (m_1*m_2)/(m_1 + m_2)
r = 0.1
I = mu * r**2

def monatomicPartitionFunction(b):
    coefficient = (L**3)/(h**3) * ((2 * np.pi * m_p) / b)**(3/2)
    summation = 0
    for j in range(0, 1000):
        summation += (2*j + 1) * np.exp(-b * (h/(2*np.pi))**2 * 1/(2*I) * j * (j + 1))

    return coefficient * summation

Z = []
for b in beta:
    z = monatomicPartitionFunction(b)
    Z.append(z)


E = - np.diff(np.log(Z)) / np.diff(beta)

plt.plot(T[:-1], E, 'r', label='Diatomic')
plt.plot(T[:-1], 1.5*k_B*T[:-1], 'g', label='3 dof')
plt.plot(T[:-1], 2.5*k_B*T[:-1], 'b', label='5 dof')
plt.legend(['Diatomic', '3 D.O.F.', '5 D.O.F.'])
plt.xlabel('Temperature $T$ [K]')
plt.ylabel('Energy $E$')
plt.title('Equation of State of Non-relativistic Diatomic Ideal Gas')
plt.show()



C_V = np.diff(E) / np.diff(T[:-1])

plt.plot(T[:-2], C_V, 'r', label='Diatomic')
plt.plot(T[:-2], 1.5*np.ones(len(T[:-2])), 'g', label='3 dof')
plt.plot(T[:-2], 2.5*np.ones(len(T[:-2])), 'b', label='5 dof')
plt.legend(['Diatomic', '3 D.O.F.', '5 D.O.F.'])
plt.xlabel('Temperature $T$ [K]')
plt.ylabel('Molar Heat Capacity $C_V$')
plt.title('Molar Heat Capacity of Non-relativistic Diatomic Ideal Gas')
plt.show()
```

Listing 2: Code for Problem 2

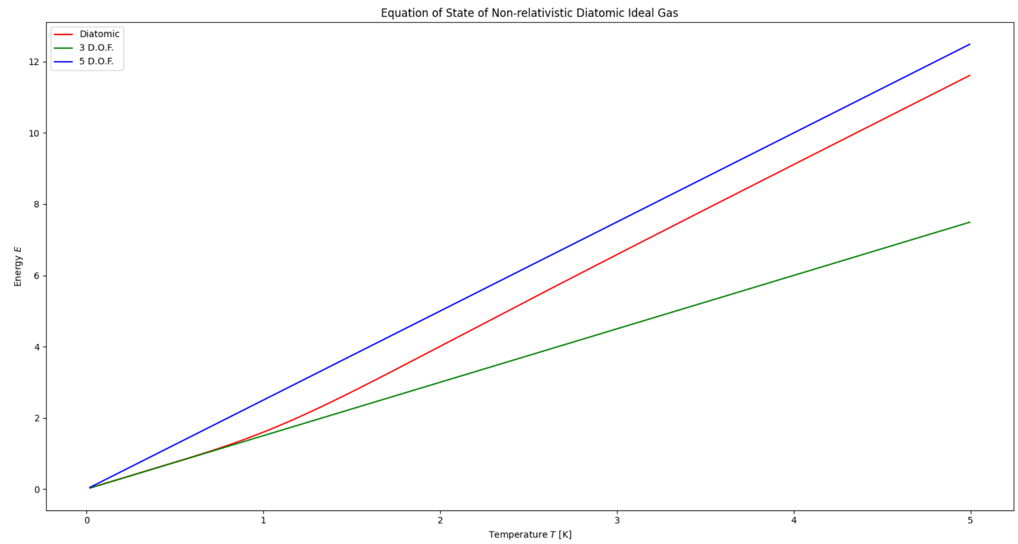

Figure 3: Plot of the energy E as a function of temperature T for a non-relativistic diatomic ideal gas.

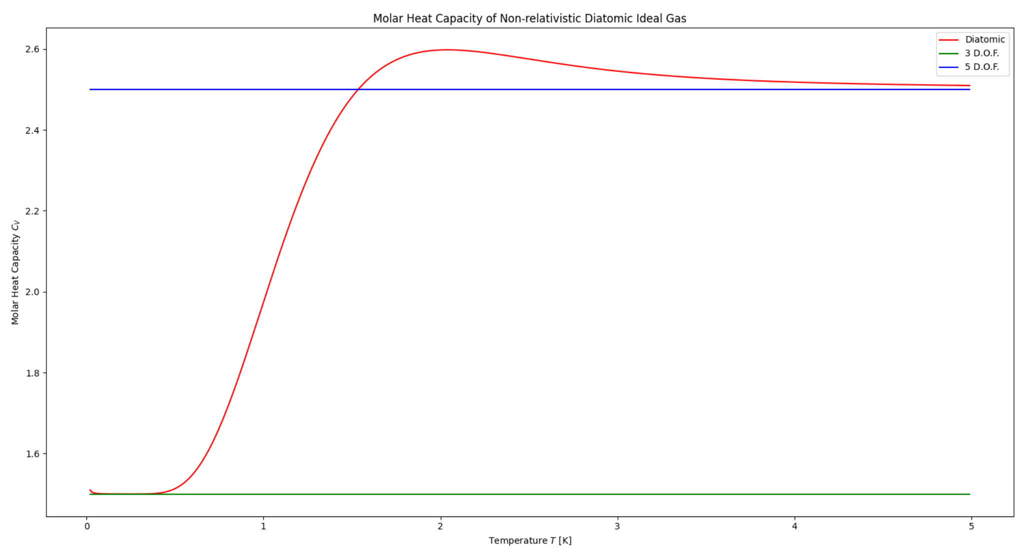

Figure 4: Plot of the heat capacity C_V as a function of temperature T for a non-relativistic diatomic ideal gas.

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Problem 3
Compute the heat capacity per particle in a two-state system with energy separation ΔE. Make a plot of this heat capacity as a function of $\beta\Delta E$. Where is it comparable to the heat capacity you would estimate for a classical system like a gas?

Solution. The partition function of a two-state system with energy separation of ΔE is given by

$$Z = 1 + \mathrm{e}^{-\beta\Delta E}.$$

The energy E is then

$$\begin{aligned} E &= -\frac{\partial \ln(Z)}{\partial \beta} \\ &= -\frac{-\Delta E \mathrm{e}^{-\beta\Delta E}}{1+\mathrm{e}^{-\beta\Delta E}} \\ &= \frac{\Delta E \mathrm{e}^{-\beta\Delta E}}{1+\mathrm{e}^{-\beta\Delta E}} \\ &= \frac{\Delta E}{\mathrm{e}^{\beta\Delta E}+1}. \end{aligned}$$

The molar heat capacity is then

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T}\right)_V \\ &= \frac{\partial E}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{\partial}{\partial \beta}\left[\frac{\Delta E}{\mathrm{e}^{\beta\Delta E}+1}\right]\left(-\frac{1}{k_B T^2}\right) \\ &= \left(-\frac{(\Delta E)^2 \mathrm{e}^{\beta\Delta E}}{\left(\mathrm{e}^{\beta\Delta E}+1\right)^2}\right)\left(-k_B\beta^2\right) \\ &= k_B\beta^2(\Delta E)^2\frac{\mathrm{e}^{\beta\Delta E}}{\left(\mathrm{e}^{\beta\Delta E}+1\right)^2}. \end{aligned}$$

Letting $x = \beta\Delta E$, we have

$$C_V = k_B\frac{x^2 e^x}{(e^x+1)^2}.$$

The heat capacity of a monatomic 1D gas is equal to $\frac{1}{2}$. Thus, when $\beta\Delta E \approx 2.4$, the heat capacity of the two-state system is comparable that of a monatomic 1D gas.
The graph of the heat capacity as a function of $\beta\Delta E$ is the following

```python
############### PROBLEM 3 ###############
x = np.linspace(0, 10, 1000)
C_V = k_B * x**2 * np.exp(x) / (np.exp(x) + 1)**2

plt.plot(x, C_V, 'r', label='Two-state')
plt.legend(['Two-State'])
plt.xlabel('$\\beta \\Delta E$')
plt.ylabel('Heat Capacity $C_V$')
plt.title('Heat Capacity of a Two-State System')
plt.show()
```

Listing 3: Code for Problem 3

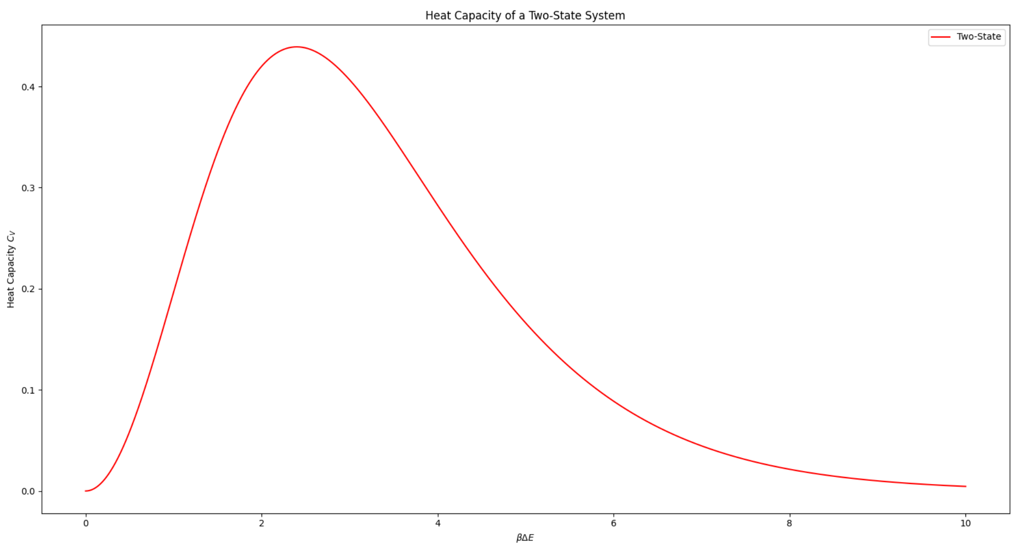

Figure 5: Plot of the heat capacity C_V as a function of $\beta \Delta E$ for a two-state system.

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Problem 4
Assuming I am technologically competent, I have attached a dataset to this assignment containing the molar heat capacity of diamond (in J/K) for a range of temperatures. Use this dataset to determine the characteristic vibrational frequency of carbon atoms in a diamond.
Are there parts of our theory of solids that predict the wrong answer?

Solution. The characteristic vibrational frequency is given by $\epsilon = \hbar\omega$. We use the equation for the heat capacity given by

$$C_V = 3Nk_B\left(\beta\epsilon\right)^2\frac{e^{\beta\epsilon}}{\left(e^{\beta\epsilon}-1\right)^2}.$$

Letting $a = \frac{\epsilon}{k_B}$ and $N = N_A$, we have

$$C_V = 3R\left(\frac{a}{T}\right)^2\frac{e^{\frac{a}{T}}}{\left(e^{\frac{a}{T}}-1\right)^2}.$$

By fitting our curve to the data, we find that $a = \frac{\epsilon}{k_B} \approx 1300\,\mathrm{K} \implies \omega = \frac{1300k_B}{\hbar} = 1.7\times10^{14}\,\mathrm{Hz}$, which matches the experimental value. Thus, our theory of solids predicts the answer to a high degree of accuracy.

```
############### PROBLEM 4 ###############
global T, C_P # Extracted from .dat file

a = 1300
N = 2
T_theory = np.linspace(0, 1100, 1000)
C_p_theory = 3 * N * k_B * (a/T_theory)**2 * np.exp(a/T_theory) / (np.exp(a/T_theory) - 1)**2

plt.scatter(T, C_p, c='k')
plt.plot(T_theory, C_p_theory, 'r')
plt.legend(['Data', 'Theory'])
plt.xlabel('Temperature $T$ [K]')
plt.ylabel('Molar Heat Capacity $C_P$ [cal/K]')
plt.title('Molar Heat Capacity of Diamond vs. Theoretical Prediction')
plt.show()
```

Listing 4: Code for Problem 4

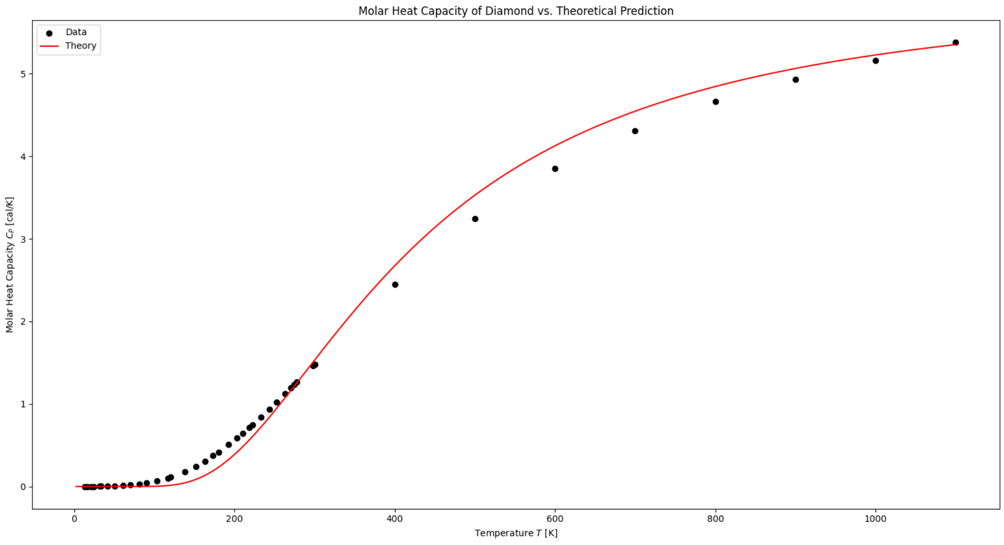

Figure 6: Plot of the experimental molar heat capacity C_V of diamond vs. the theoretical prediction.

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