Contents:

This notebook has two sections.

- Distribution Functions
- Specific Heat References

To learn more about each of the functions and libraries used, use the links in the References section. Import python modules (pre-defined functions and libraries) numpy, scipy and matplotlib.

Distribution Funtions

The codes to implement and fit the three distribution functions in statistical physics.

- Maxwell-Boltzmann
- Fermi-Dirac
- Bose-Einstein

Specific Heat

This section focuses on the specific heat of solids and compares the results from

- Dulong Petit law
- Einstein distribution function
- Debye distribution function

In [1]:
```
import numpy as np
from scipy.integrate import quad
import matplotlib.pyplot as plt
```

In [2]:
```
newparams = {
     'axes.labelsize': 10, 'axes.linewidth': 1.5,
    'savefig.dpi': 300,
    'lines.linewidth': 2,
    'legend.frameon': True,
    'legend.handlelength': 0.7}

plt.rcParams.update(newparams)
```

What are python functions?

A function is a block of code which only runs when it is called.

You can pass data, known as parameters, into a function.

A function can return data as a result.

In [3]:
```
def square(num):
    """This is a function to
    calculate the square of a
```

```
    given number. Here num is the
    input or parameter to the
    function square()"""

    output = num**2

    return output
```

In [4]:
```
square(3)
```

Out[4]: 9

In [5]:
```
square(25)
```

Out[5]: 625

The function needs to be defined before it is called/used in the code.

Once the function has been defined, it can be called any time and in any order.

In [6]:
```
cube(6)
```

```
---------------------------------------------------------------------------
NameError                                 Traceback (most recent call last)
<ipython-input-6-a85afd6b173b> in <module>
----> 1 cube(6)

NameError: name 'cube' is not defined
```

Since the function "cube" has not been defined it returns an error.

In [ ]:
```
def cube(num):
    """This is a function to
    calculate the square of a
    given number. Here num is the
    input or parameter to the
    function cube()"""

    return num**3
```

In [ ]:
```
cube(6)
```

In [ ]:
```
square(12)
```

Some pre-defined functions that are used in this notebook:

- np.exp(): calculates the exponential value.
- np.linspace(): return evenly spaced numbers over a specified interval. returns num evenly spaced samples, calculated over the interval [start, stop].
- np.ones(): return a new array of given shape and type, filled with ones.
- np.zeros(): return a new array of given shape and type, filled with zeros.
- enumerate(): returns an iterable object.
- quad(): computes a definite integral of a function from a to b (possibly infinite interval). The first item of the output list is the integral value. The second entry is the estimate of the absolute error in the result.

In [7]:
```
np.exp(2)
```

Out[7]:
```
7.38905609893065
```

In [8]:
```
np.linspace(1, 10, 10)
```

Out[8]:
```
array([ 1.,  2.,  3.,  4.,  5.,  6.,  7.,  8.,  9., 10.])
```

In [9]:
```
np.linspace(1, 10, 50)
```

Out[9]:
```
array([ 1.        ,  1.18367347,  1.36734694,  1.55102041,  1.73469388,
        1.91836735,  2.10204082,  2.28571429,  2.46938776,  2.65306122,
        2.83673469,  3.02040816,  3.20408163,  3.3877551 ,  3.57142857,
        3.75510204,  3.93877551,  4.12244898,  4.30612245,  4.48979592,
        4.67346939,  4.85714286,  5.04081633,  5.2244898 ,  5.40816327,
        5.59183673,  5.7755102 ,  5.95918367,  6.14285714,  6.32653061,
        6.51020408,  6.69387755,  6.87755102,  7.06122449,  7.24489796,
        7.42857143,  7.6122449 ,  7.79591837,  7.97959184,  8.16326531,
        8.34693878,  8.53061224,  8.71428571,  8.89795918,  9.08163265,
        9.26530612,  9.44897959,  9.63265306,  9.81632653, 10.        ])
```

In [10]:
```
np.ones(10)
```

Out[10]:
```
array([1., 1., 1., 1., 1., 1., 1., 1., 1., 1.])
```

In [11]:
```
np.zeros(8)
```

Out[11]:
```
array([0., 0., 0., 0., 0., 0., 0., 0.])
```

In [12]:
```
enumerate([2, 8, 4, 10, 3, 19, 6])
```

Out[12]:
```
<enumerate at 0x15c7ea15600>
```

In [13]:
```
for i, j in enumerate([2, 8, 4, 10, 3, 19, 6]):
    print('index/position of the item in the list is:', i,
          'and corresponding item in the list is:', j)
```

```
index/position of the item in the list is: 0 and corresponding item in the list is: 2
index/position of the item in the list is: 1 and corresponding item in the list is: 8
index/position of the item in the list is: 2 and corresponding item in the list is: 4
index/position of the item in the list is: 3 and corresponding item in the list is: 10
index/position of the item in the list is: 4 and corresponding item in the list is: 3
index/position of the item in the list is: 5 and corresponding item in the list is: 19
index/position of the item in the list is: 6 and corresponding item in the list is: 6
```

For the integral, calculate

$$\int_0^2 x^3 dx = \frac{x^4}{4}|_0^2 = 4$$

In [14]:
```
quad(lambda x: x**3, 0, 2)
```

Out[14]:
```
(4.0, 4.440892098500626e-14)
```

This shows that the absolute error in calculating the above definite integral was 4.4×10^{-14} (extremely low error,high accuracy).

Maxwell-Boltzmann distribution function

Maxwell–Boltzmann statistics describes the average distribution of non-interacting material particles over various energy states in thermal equilibrium. These particles are identical and treated as distinguishable.

The distribution function is given by:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T}}$$

where E is the energy state,

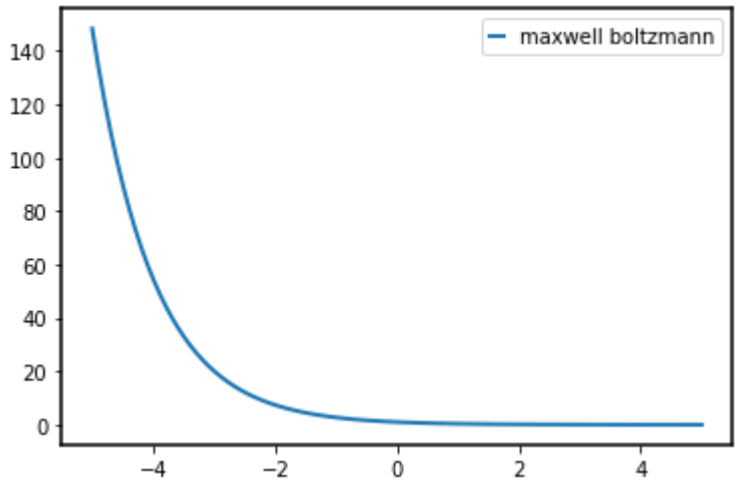
μ is the chemical potential,

k_B is the Boltzmann constant, $1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$

T is the temperature (in Kelvins)

In [15]:
```
def maxwell_boltzmann(x):

    mb = (1./(np.exp(x)))

    return mb
```

In [16]:
```
x = np.linspace(-5, 5, 100)
mb_func = maxwell_boltzmann(x)

plt.figure()
plt.plot(x, mb_func, label='maxwell boltzmann')
plt.legend(loc='best')
plt.show()
```



Fermi-Dirac distribution function

Fermi-Dirac distribution applies to the physics of a system consisting of many identical particles that obey the Pauli exclusion principle. Fermi–Dirac statistics applies to identical and indistinguishable particles with half-integer spin (1/2, 3/2, etc.), called fermions, in thermodynamic equilibrium.

The distribution function is given by:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

where E is the energy state,

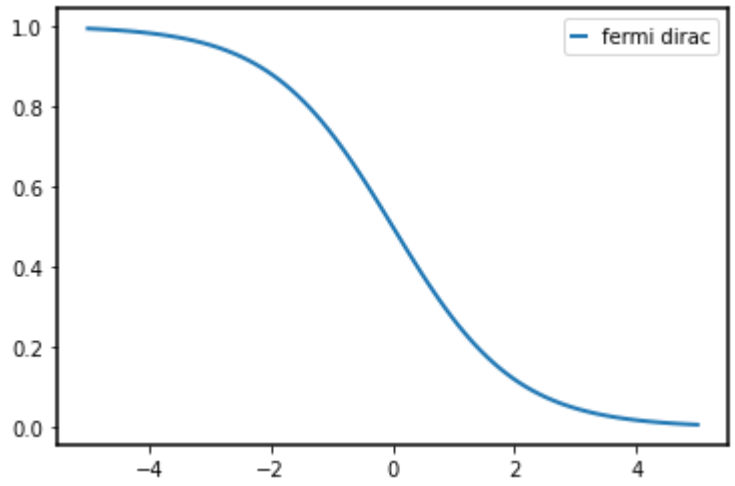
μ is the chemical potential,

k_B is the Boltzmann constant, $1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$

T is the temperature (in Kelvins)

In [17]:
```
def fermi_dirac(x):

    fd = (1./(np.exp(x)+1))

    return fd
```

In [18]:
```
x = np.linspace(-5, 5, 100)
fd_func = fermi_dirac(x)

plt.figure()
plt.plot(x, fd_func, label='fermi dirac')
plt.legend(loc='best')
plt.show()
```



Bose-Einstein distribution function

The Bose–Einstein is a type of quantum statistics that applies only to those particles not limited to single occupancy of the same state, particles have integer values of spin (0, 1, 2 etc.) and are named bosons. There must also be no significant interaction between the particles. These particles are also identical and indistinguishable.

The distribution function is given by:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1}$$

where E is the energy state,

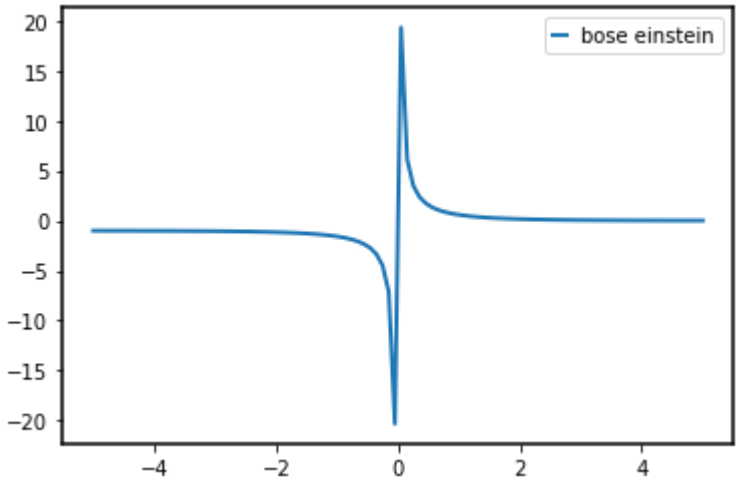
μ is the chemical potential,

k_B is the Boltzmann constant, $1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$

T is the temperature (in Kelvins)

In [19]:
```
def bose_einstein(x):

    bose_result = (1/(np.exp(x)-1))

    return bose_result
```

In [20]:
```
x = np.linspace(-5, 5, 100)
be = bose_einstein(x)

plt.figure()
plt.plot(x, be, label ='bose einstein')
plt.legend(loc='best')
plt.show()
```



Plotting all 3 dustribution together

Plot the following functions with energy at different temperatures:

a) Maxwell-Boltzmann distribution

b)Fermi-Dirac distribution

c) Bose-Einstein distribution

Define a general function:

$$f(E) = \frac{1}{(exp((E-\mu)/k_B T) + a)}$$

Plot this function for different E and T values.

- $a = 0$ for Maxwell Boltzmann

- $a = +1$ for Fermi Dirac
- $a = -1$ for Bose Einstein

In [21]:
```
## define the constants

e = 1.6e-19    #electric charge
k = 1.38e-23    #Boltzmann constant(joule per kelvin)
```

In [22]:
```
def func(T, u, a):
    """ This is the general equation,
    for a given chemical potential u,
    with the input variable a=0,
    for Maxwell-Boltxmann distribution;
    input variable a=-1,
    for Bose-Einstein; and
    input variable a=+1,
    for Fermi-Dirac """

    return 1/((np.exp(((E-u)*e)/(k*T)))+a)
```

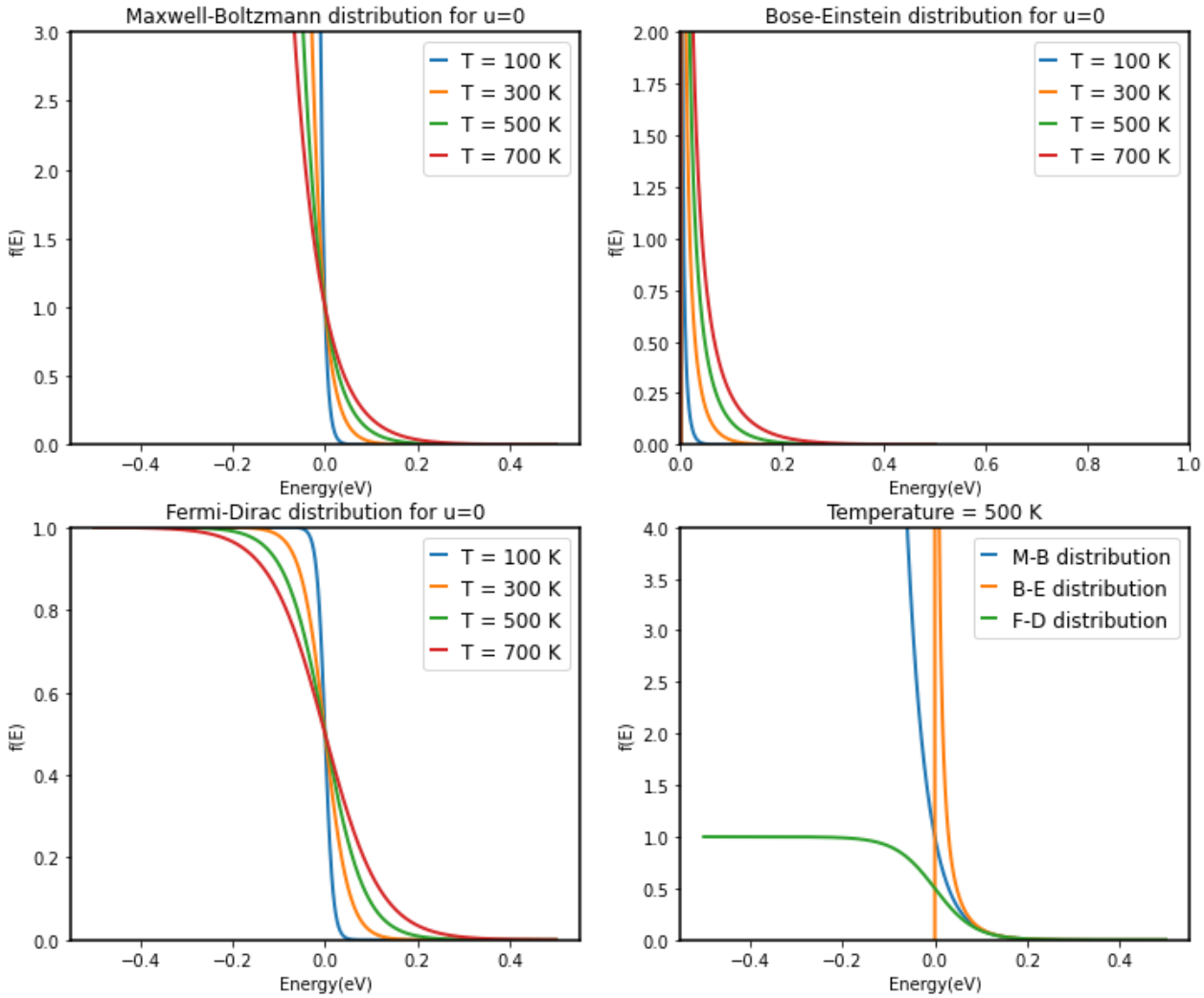
Plots for $\mu = 0$ and energy range [-0.5, 0.5] for 4 different temperatures: 100K, 200K, 500K and 700K

In [23]:
```
E = np.linspace(-0.5, 0.5, 1000)    #energy range
u1 = 0     #considering chemeical potential of the substance is zero
```

In [24]:
```
plt.figure(figsize=(12, 10))

plt.suptitle('Plot of the following functions at different temperatures',
             size = 16,color='b')


plt.subplot(2,2,1)
plt.plot(E, func(100, u1, 0),label='T = 100 K')
plt.plot(E, func(300, u1, 0),label='T = 300 K')
plt.plot(E, func(500, u1, 0),label='T = 500 K')
plt.plot(E, func(700, u1, 0),label='T = 700 K')
plt.ylim(0,3)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.legend(loc='best',prop={'size':12})
plt.title('Maxwell-Boltzmann distribution for u=0')


plt.subplot(2,2,2)
plt.plot(E, func(100, u1, -1),label='T = 100 K')
plt.plot(E, func(300, u1, -1),label='T = 300 K')
plt.plot(E, func(500, u1, -1),label='T = 500 K')
plt.plot(E, func(700, u1, -1),label='T = 700 K')
plt.xlim(0,1)
plt.ylim(0,2)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.legend(loc='best',prop={'size':12})
plt.title('Bose-Einstein distribution for u=0')


plt.subplot(2,2,3)
plt.plot(E, func(100, u1, +1),label='T = 100 K')
plt.plot(E, func(300, u1, +1),label='T = 300 K')
```

```
plt.plot(E, func(500, u1, +1),label='T = 500 K')
plt.plot(E, func(700, u1, +1),label='T = 700 K')
plt.legend(loc='best',prop={'size':12})
plt.ylim(0,1)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.title('Fermi-Dirac distribution for u=0')


plt.subplot(2,2,4)
plt.plot(E, func(500, u1, 0),label='M-B distribution')
plt.plot(E, func(500, u1, -1),label='B-E distribution')
plt.plot(E, func(500, u1, +1),label='F-D distribution')
plt.legend(loc='best',prop={'size':12})
plt.ylim(0,4)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.title('Temperature = 500 K')

plt.show()
```

Plot of the following functions at different temperatures



Plots for $\mu = 12$ and energy range [-2, 2] for 4 different temperatures: 100K, 200K, 500K and 700K

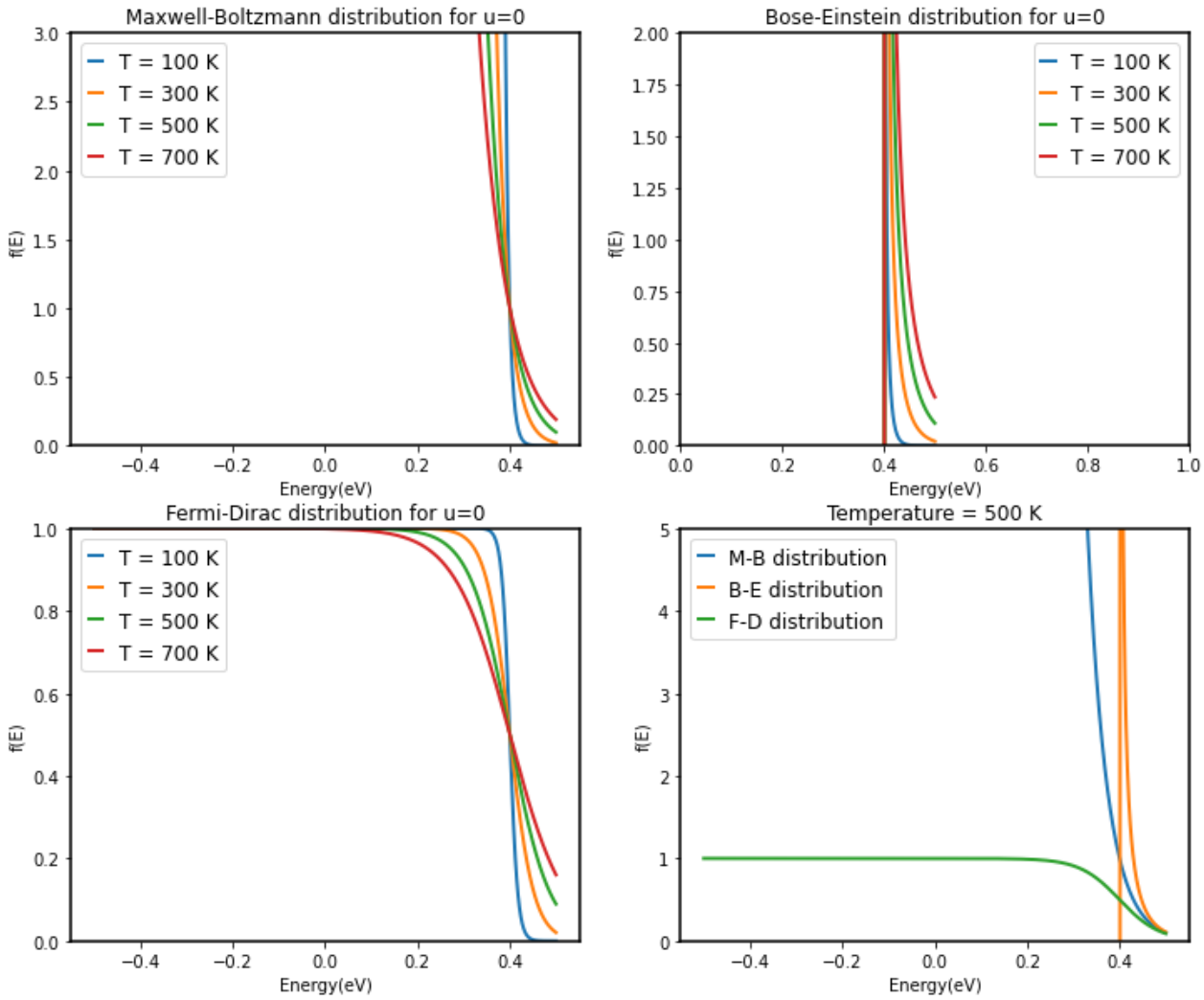
In [25]:
```
E = np.linspace(-0.5, 0.5, 1000)    #energy range
```

```
u2 = 0.4    #considering chemeical potential of the substance is zero
```

In [26]:

```
plt.figure(figsize=(12, 10))

plt.suptitle('Plot of the following functions at different temperatures for $\mu = 12$'
             size = 16,color='b')


plt.subplot(2,2,1)
plt.plot(E, func(100, u2, 0),label='T = 100 K')
plt.plot(E, func(300, u2, 0),label='T = 300 K')
plt.plot(E, func(500, u2, 0),label='T = 500 K')
plt.plot(E, func(700, u2, 0),label='T = 700 K')
plt.ylim(0,3)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.legend(loc='best',prop={'size':12})
plt.title('Maxwell-Boltzmann distribution for u=0')


plt.subplot(2,2,2)
plt.plot(E, func(100, u2, -1),label='T = 100 K')
plt.plot(E, func(300, u2, -1),label='T = 300 K')
plt.plot(E, func(500, u2, -1),label='T = 500 K')
plt.plot(E, func(700, u2, -1),label='T = 700 K')
plt.xlim(0,1)
plt.ylim(0,2)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.legend(loc='best',prop={'size':12})
plt.title('Bose-Einstein distribution for u=0')


plt.subplot(2,2,3)
plt.plot(E, func(100, u2, +1),label='T = 100 K')
plt.plot(E, func(300, u2, +1),label='T = 300 K')
plt.plot(E, func(500, u2, +1),label='T = 500 K')
plt.plot(E, func(700, u2, +1),label='T = 700 K')
plt.legend(loc='best',prop={'size':12})
plt.ylim(0,1)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.title('Fermi-Dirac distribution for u=0')


plt.subplot(2,2,4)
plt.plot(E, func(500, u2, 0),label='M-B distribution')
plt.plot(E, func(500, u2, -1),label='B-E distribution')
plt.plot(E, func(500, u2, +1),label='F-D distribution')
plt.legend(loc='best',prop={'size':12})
plt.ylim(0,5)
plt.xlabel('Energy(eV)')
plt.ylabel('f(E)')
plt.title('Temperature = 500 K')

plt.show()
```

Plot of the following functions at different temperatures for $\mu = 12$



Specific Heat

- Plot Dulong-Petit law
- Einstein distribution function
- Debye distribution function for high temperature and low temperature and compare them for the two cases.

Dulong Petit law

Dulong and Petit found that the heat capacity of a mole of many solid elements is about $3N_Ak_B$ (or $3R$),

where

R is the universal gas constant, $8.314 JK^{-1}mol^{-1}$,

N_A is the Avogardro's number, 6.023×10^{23},

k_B is the Bolzmann constant, $1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$

Einstein distribution function

The speific heat distribution is given by

$$C_V = 3N_A k_B \left(\frac{\varepsilon}{k_B T} \right)^2 \frac{e^{\varepsilon / k_B T}}{\left(e^{\varepsilon / k_B T} - 1 \right)^2}$$

$$C_V = 3N_A k_B \left(\frac{T_E}{T} \right)^2 \frac{e^{T_E / T}}{\left(e^{T_E / T} - 1 \right)^2}$$

where

Einstein temperature, $T_E = \varepsilon / k_B = \hbar w / k_B$ and $\varepsilon = \hbar \omega$ is the quantum of energy, ω is the vibrational frequency of the phonons.

Although the Einstein model of the solid predicts the heat capacity accurately, in the high temperature limit,

$$\lim_{T \to \infty} C_V = 3N_A k_B$$

Debye distribution function

Debye distribution function is used to estimate the phonon contribution to the specific heat (heat capacity) in a solid.

The Debye model correctly predicts the low temperature dependence of the heat capacity, which is proportional to T^3 – the Debye T^3 law. Just like the Einstein model, it also recovers the Dulong–Petit law at high temperatures.

$$C_V = 9N_A k_B \left(\frac{T}{T_D} \right)^3 \int_0^{T_D / T} \frac{x^4 e^x}{e^x - 1} dx$$

where T_D is the Debye temperature

Low temperature limit

$$\lim_{T \to 0} C_V = 12 / 5 \pi^4 N_A k_B (T / T_D)^3$$

High temperature limit

$$\lim_{T \to \infty} C_V = 3N_A k_B$$

In [27]:
```
## define the contants

h = 6.626e-34     # Planck's constant
k = 1.38e-23      # Boltzmann constant
NA = 6.23e23      # Avogadro's number
```

In [28]:
```
def dp_law(temp):
    dp = 3*NA*k* np.ones(len(temp))
    return dp
```

In [29]:
```
def einstein_dist(temp, te):
    en = 3*NA*k*(te/temp)**2 * (np.exp(te/temp)/(np.exp(te/temp) - 1)**2)
    return en
```

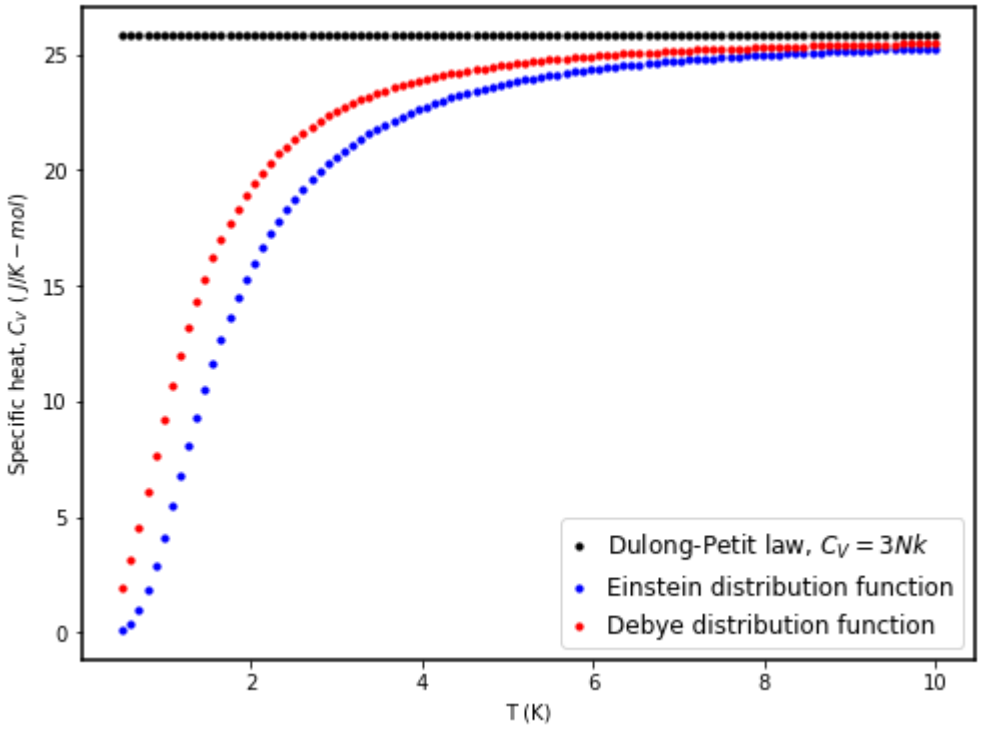
In [30]:
```
def debye_dist(temp, td):

    debye = np.zeros(len(temp))

    for i, t in enumerate(temp):
        integral = quad(lambda x : x**4*np.exp(x)/(np.exp(x) - 1)**2, 0, (td/t))[0]

        debye[i] = 9*NA*k*(t/td)**3*integral
    return debye
```

In [31]:
```
# Eintsein and Debye temperatures for solid 1 ()

Te1 = 5          # Einstein temperature, hw/k (either need w or Te)
Td1 = 5          # Debye temperature, hw/k (either need w or Td)
```

In [32]:
```
T = np.linspace(0.5, 10, 100)
```

In [33]:
```
plt.figure(figsize=(8,6))

plt.scatter(T, dp_law(T), label = 'Dulong-Petit law, $C_V = 3Nk$', s = 10, color = 'k')
plt.scatter(T, einstein_dist(T, Te1), label = 'Einstein distribution function', s = 10,
plt.scatter(T, debye_dist(T, Td1), label = 'Debye distribution function', s = 10, color
plt.xlabel('T (K)')
plt.ylabel('Specific heat, $C_V$ $($ $J/K-mol)$')
plt.legend(loc='best',prop={'size':12})
```

Out[33]:
```
<matplotlib.legend.Legend at 0x15c7ee6e9d0>
```

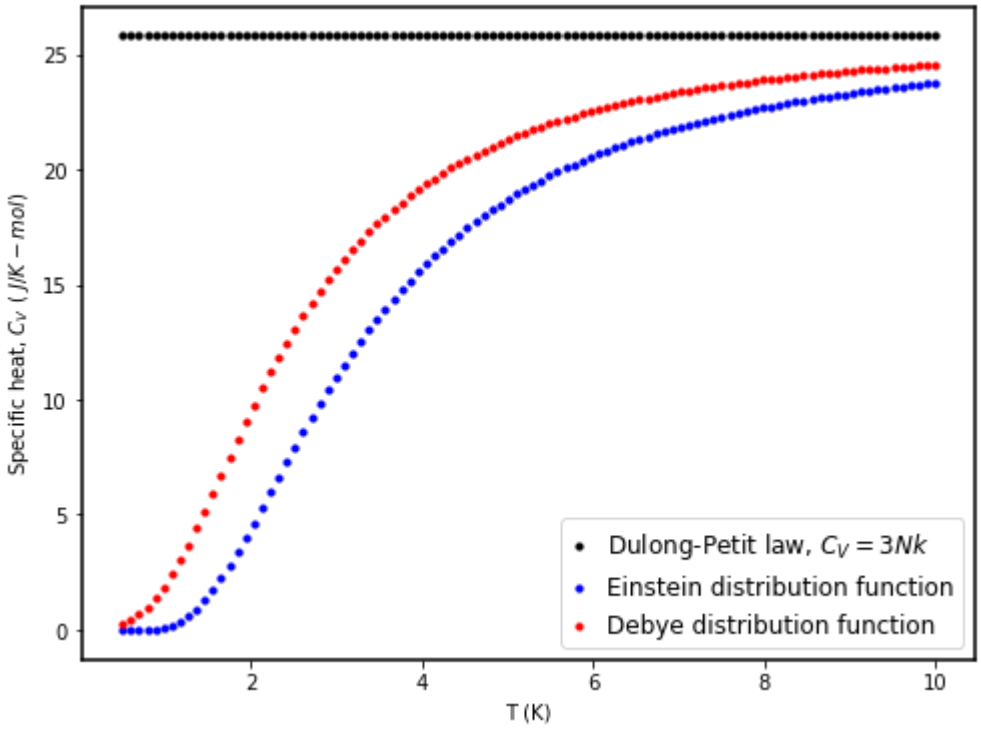


In [34]:
```
# Eintsein and Debye temperatures for solid 1 ()

Te2 = 10          # Einstein temperature, hw/k (either need w or Te)
Td2 = 10           # Debye temperature, hw/k (either need w or Td)
```

In [35]:
```
T = np.linspace(0.5, 10, 100)
```

In [36]:
```
plt.figure(figsize=(8,6))

plt.scatter(T, dp_law(T), label = 'Dulong-Petit law, $C_V = 3Nk$', s = 10, color = 'k')
plt.scatter(T, einstein_dist(T, Te2), label = 'Einstein distribution function', s = 10,
plt.scatter(T, debye_dist(T, Td2), label = 'Debye distribution function', s = 10, color
plt.xlabel('T (K)')
plt.ylabel('Specific heat, $C_V$ $($ $J/K-mol)$')
plt.legend(loc='best',prop={'size':12})
```

Out[36]:
```
<matplotlib.legend.Legend at 0x15c7f273df0>
```



Debye - low and high temperature comparison

At high temperatures, $(T >> T_D, \rightarrow \frac{T_D}{T} << 1)$. So, $C_V = 3N_A k_B$.

At low temperature, $(T << T_D, \rightarrow \frac{T_D}{T} >> 1)$. So, $C_V = \frac{12}{5}\pi^4 N_A k_B \left(\frac{T}{T_D}\right)^3$

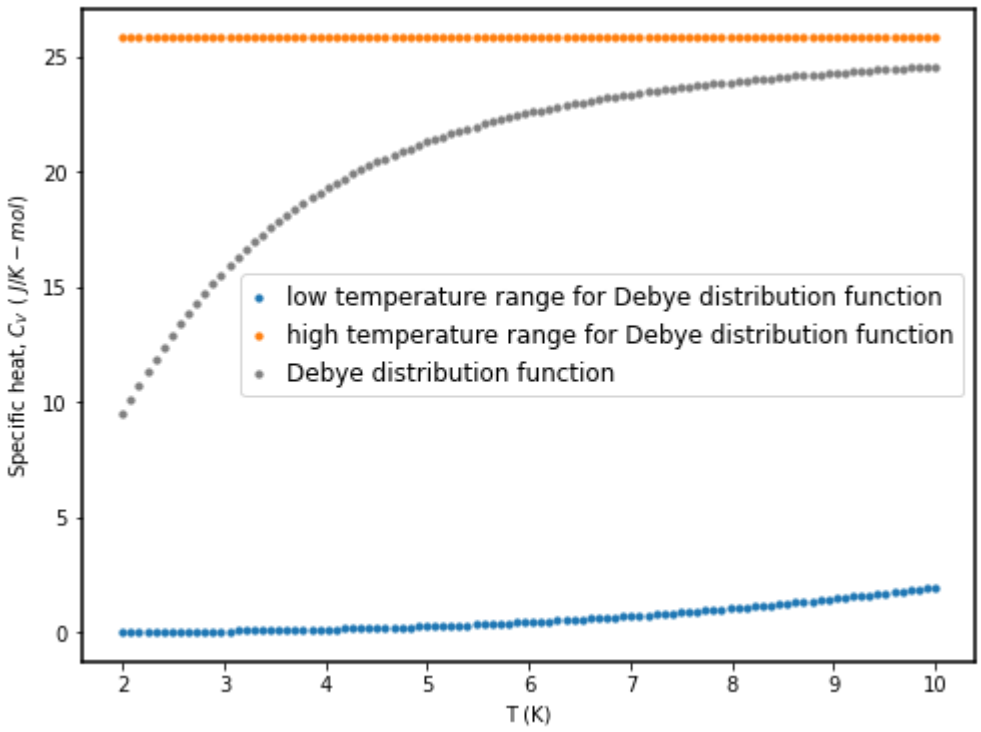
In [37]:
```
def low_debye(temp, td):

    debye = 12/5 *(np.pi)**4 *(NA*k) * (temp/td)**3

    return debye
```

In [38]:
```
def debye_high(temp):

    debye = 3*NA*k* np.ones(len(temp))

    return debye
```

In [39]:
```
T = np.linspace(2, 10, 100)
Td_low = 0.00001                # this is the high temperature range (i.e., Td << T)
Td_high = 100                   # this is the low temperature range (i.e., Td >> T)
```

In [40]:
```
plt.figure(figsize=(8,6))

plt.scatter(T, debye_dist(T, Td_high),
            label = 'low temperature range for Debye distribution function', s = 10)
plt.scatter(T, debye_dist(T, Td_low),
            label = 'high temperature range for Debye distribution function', s = 10)
plt.scatter(T, debye_dist(T, Td2), label = 'Debye distribution function', s = 10, color

plt.xlabel('T (K)')
plt.ylabel('Specific heat, $C_V$ $($ $J/K-mol)$')
plt.legend(loc='best',prop={'size':12})
```

Out[40]: <matplotlib.legend.Legend at 0x15c7ed0cd90>



References:

1. python numpy
2. python matplotlib
3. numpy linspace
4. numpy exp
5. enumerate
6. scipy quad
7. numpy zeros
8. numpy ones

In [ ]: