TTS Data A HDPE Resins 5 temperatures

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In [1]:
```
# PYTHON LIBRARIES
%matplotlib inline

import pandas as pd
import numpy as np
import datetime
import matplotlib as mpl
import matplotlib.dates as mdates
import matplotlib.pyplot as plt
import warnings
warnings.filterwarnings('ignore')

from adjustText import adjust_text
from sklearn.preprocessing import LabelEncoder
number = LabelEncoder()
from pandas.plotting import register_matplotlib_converters
register_matplotlib_converters()
from matplotlib.axes._axes import _log as matplotlib_axes_logger
matplotlib_axes_logger.setLevel('ERROR')
from sklearn.linear_model import LinearRegression
```

---

function to plot a pandas dataframe

In [2]:
```python
def plot(df, pltname, plotGs=True):
    # PLOT SETUP
    scale = 6;
    fig   = plt.figure(figsize=(3*scale, 2*scale));
    plt.rc('xtick', labelsize=15)
    plt.rc('ytick', labelsize=15)
    plt.tight_layout();

    for i in range(0,len(df.columns),3):
        # Define x axis as the date axis
        x_str  = df.columns[i];   x_units = r'$[\frac{rad}{s}]$';
        y1_str = df.columns[i+1]; y_units = r'$[Pa \cdot s]$';
        y2_str = df.columns[i+2];

        # Remove NANs from interesting x,y data
        df_fil = pd.DataFrame(df);
        df_fil = df_fil.dropna(subset=[x_str, y1_str, y2_str]);

        # Stablish the plot area
        ax0 = plt.gca()

        # Extract data from a specific country
        x  = df_fil.iloc[:][x_str];
        y1 = df_fil.iloc[:][y1_str];
        y2 = df_fil.iloc[:][y2_str];

        # Plot a curve to join the data points
        #plt.plot(x, y) #, label="B")
        if plotGs:
            plt.scatter(x, y1, s=45, marker='o', label=r'$G^\prime(\omega)$' + ' ' + df.columns[i+1].split('_')[1])
            plt.scatter(x, y2, s=45, marker='s', label=r'$G^{\prime\prime}(\omega)$' + ' ' + df.columns[i+2].split('_'
)[1])
            plt.plot(x, y1, linewidth=1, linestyle='-.')
            plt.plot(x, y2, linewidth=1, linestyle='-.')
        else:
            plt.scatter(x, y2/y1, s=45, marker='^', label=df.columns[i+1].split('_')[1])
            plt.plot(x, y2/y1, linewidth=1, linestyle=':')

    # Show the plot lengend to link colors and polymer names
    handles, labels = ax0.get_legend_handles_labels();
    lgd = dict(zip(labels, handles));
```

```python
    # fig.autofmt_xdate();
    ax0.set_xlabel(r'$\omega$' + '     ' + x_units, fontsize=24);
    if plotGs:
        ax0.set_ylabel(r'$G^\prime(\omega)$'  + ' and ' +  r'$G^{\prime\prime}(\omega)$' + '     ' + y_units, fontsize=
24);
    else:
        ax0.set_ylabel(r'$tan \delta$' + '     ' + y_units, fontsize=24);

    for tick in ax0.xaxis.get_major_ticks():
        tick.label.set_fontsize(18)
    for tick in ax0.yaxis.get_major_ticks():
        tick.label.set_fontsize(18)

    ax0.tick_params(which='both', direction='in', length=5, width=2, bottom=True, top=True, left=True, right=True)

    # Display main plot
    plt.yscale('log');
    plt.xscale('log');
    plt.legend(lgd.values(), lgd.keys(), prop={'size': 18}, loc="best");
    plt.title(pltname, size=24);
    plt.savefig(pltname + '.png', dpi=200, bbox_inches='tight');
    plt.show();
    mpl.rcParams.update(mpl.rcParamsDefault); # Recover matplotlib defaults
```

WLF (Williams Landel Ferry)

$$loga_T = \frac{-c_1\left(T - T_0\right)}{c_2 + \left(T - T_0\right)}$$

where:
c_1 and c_2 are empirical constants
T is the temperature of interest
T_0 is the reference temperature
a_T is the amount by which the time has to be shifted to get the same result at T as in T_0

In [3]:
```python
def _a_T(T, T_0, c_1, c_2):
    if T != T_0:
        nume = - c_1 * (T - T_0);
        deno = c_2 + (T - T_0);
        exp  = nume / deno;
        a_T  = 10**exp;
    else:
        a_T = 1;
    return a_T;

def _invTninvT0(T,T_0):
    return (1/T)-(1/T_0)
```

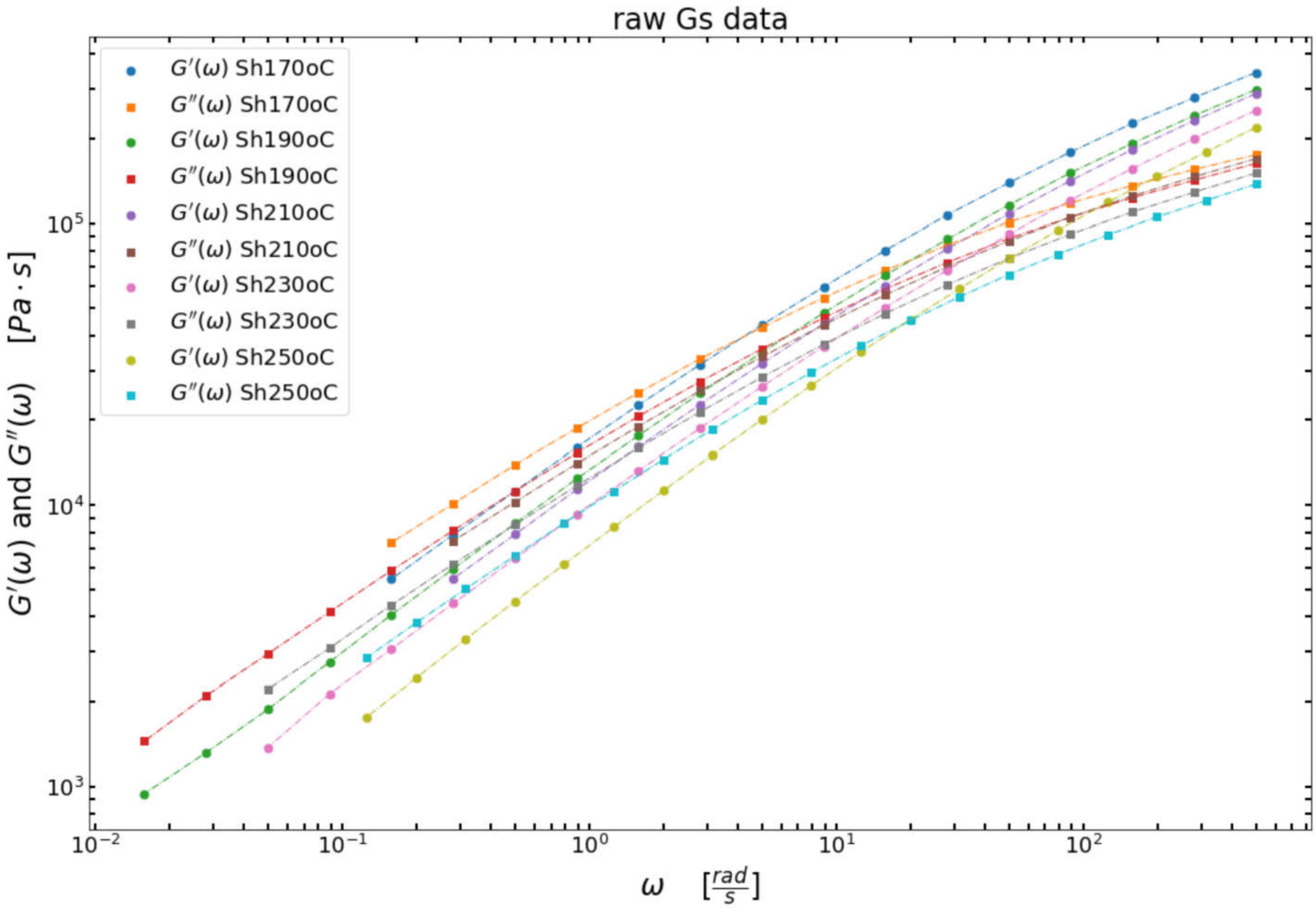
Arrhenius

$$a_T = e^{\left[\frac{E_H}{R}\left(\frac{1}{T+273} - \frac{1}{T_0+273}\right)\right]}$$

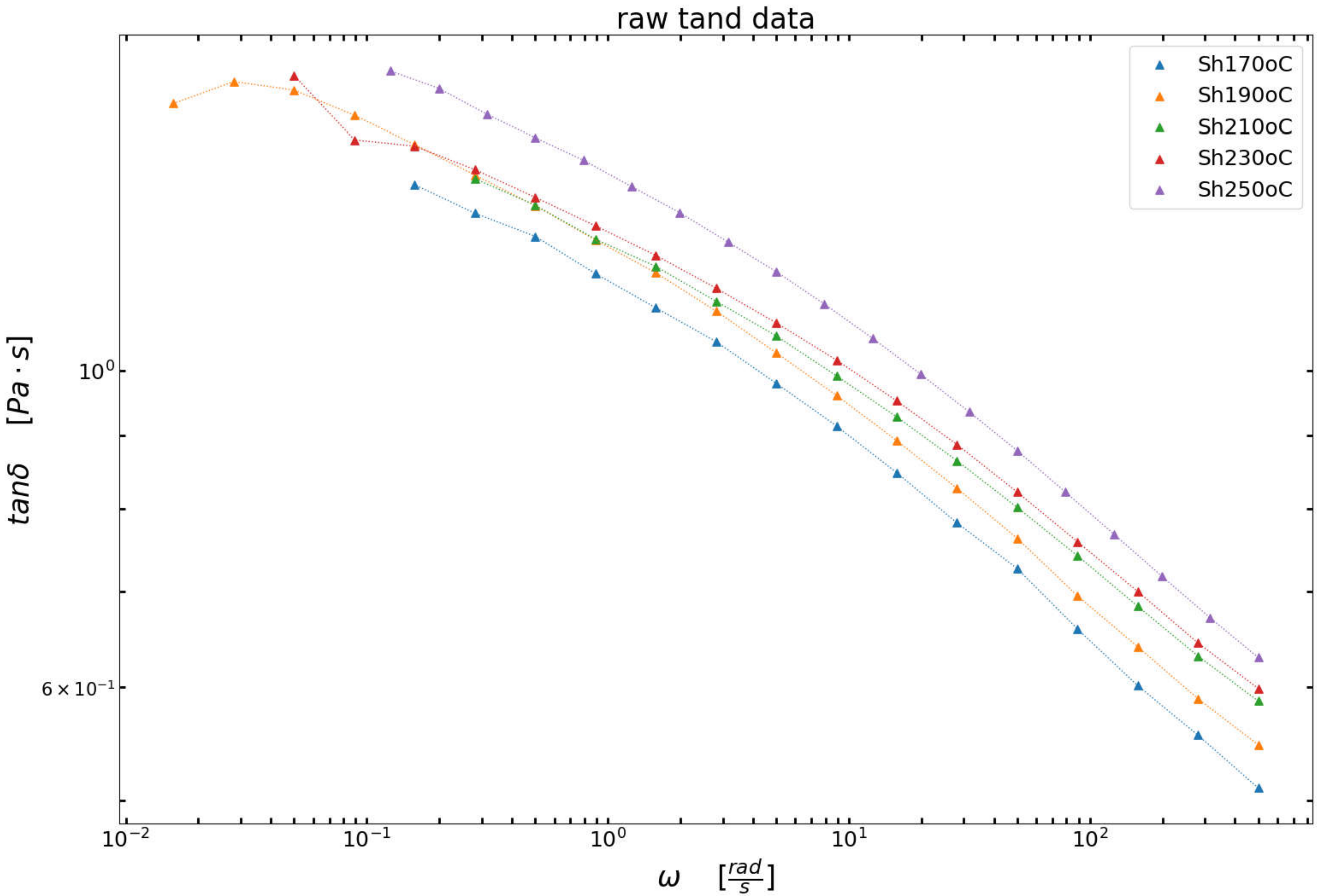
In [4]:
```python
def _Arrhenius(EH, T, T0):
    frac  = EH / 8.314;
    paren = (1/(T0+273.15)) - (1/(T+273.15));
    exp = frac * paren;
    return np.exp(exp);
```

read .csv with the provided frequency, G', and G'' data

In [5]:
```
df_raw = pd.read_csv("./data.csv", delimiter=",");
plot(df_raw, "raw Gs data", True)
plot(df_raw, "raw tand data", False)
print("./data.csv"); display(df_raw.head(10));
```



raw Gs data
$G'(\omega)$ Sh170oC
$G''(\omega)$ Sh170oC
$G'(\omega)$ Sh190oC
$G''(\omega)$ Sh190oC
$G'(\omega)$ Sh210oC
$G''(\omega)$ Sh210oC
$G'(\omega)$ Sh230oC
$G''(\omega)$ Sh230oC
$G'(\omega)$ Sh250oC
$G''(\omega)$ Sh250oC
$G'(\omega)$ and $G''(\omega)$ $[Pa \cdot s]$
ω $[\frac{rad}{s}]$
10^{3}
10^{4}
10^{5}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}


raw tand data
Sh170oC
Sh190oC
Sh210oC
Sh230oC
Sh250oC
10^0
6×10^{-1}
$tan\delta \quad [Pa \cdot s]$
10^{-2}
10^{-1}
10^0
10^1
10^2
$\omega \quad [\frac{rad}{s}]$

./data.csv

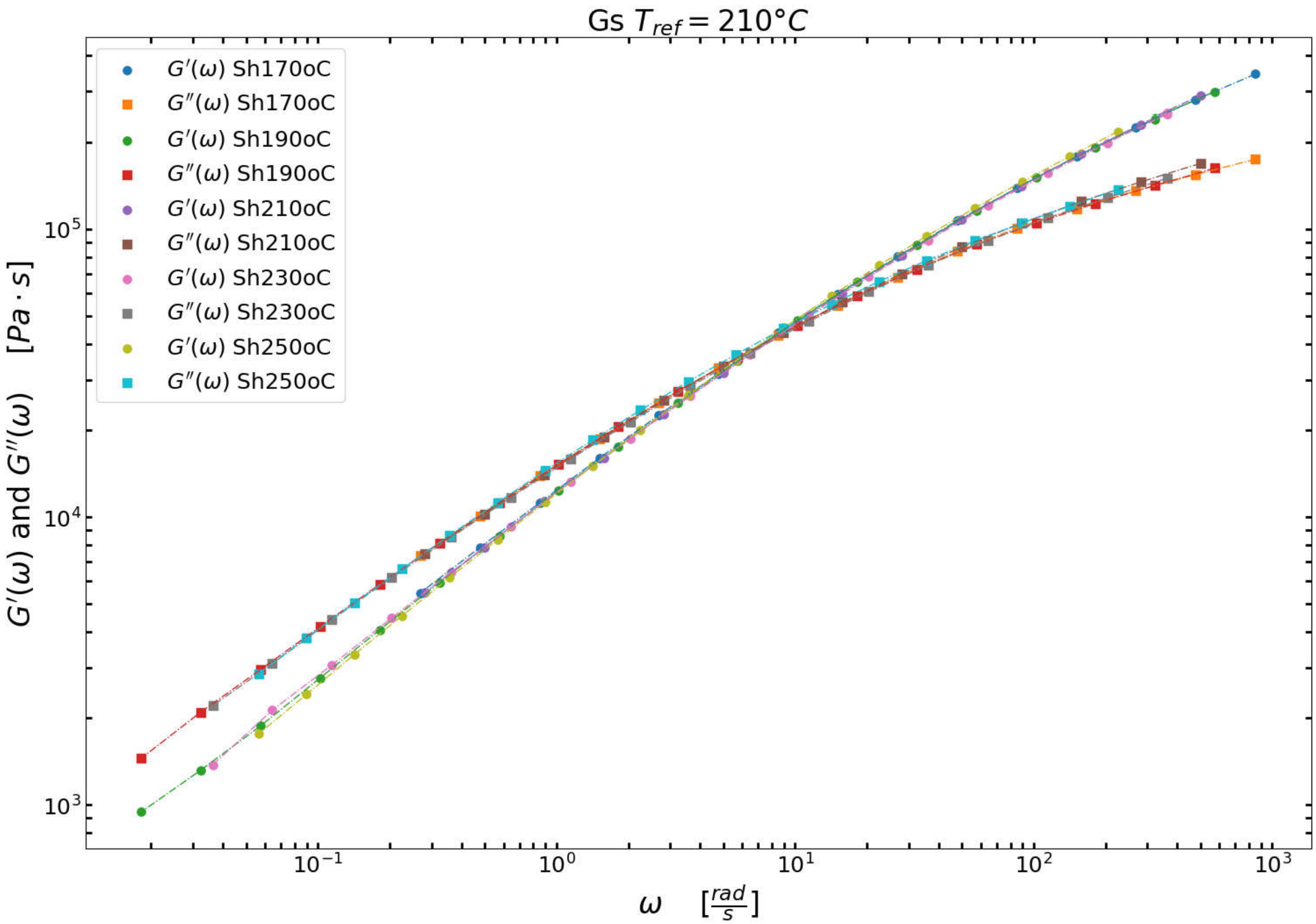
	frecuencia_Sh170oC	G1_Sh170oC	G2_Sh170oC	frecuencia_Sh190oC	G1_Sh190oC	G2_Sh190oC	frecuencia_Sh210oC_ref	G1_Sh210oC_ref	G2
0	500.00	343000.0	175000.0	500.00	298000.0	163000.0	500.00000	288545.0	
1	281.00	279000.0	155000.0	281.00	241000.0	142000.0	281.17200	231412.0	
2	158.00	226000.0	136000.0	158.00	192000.0	123000.0	158.11700	182623.0	
3	88.90	179000.0	118000.0	88.90	151000.0	105000.0	88.91600	141545.0	
4	50.00	139000.0	101000.0	50.00	116000.0	88500.0	50.00200	108073.0	
5	28.10	107000.0	83700.0	28.10	87900.0	72700.0	28.11870	81183.4	
6	15.80	80300.0	68100.0	15.80	65500.0	58500.0	15.81250	60144.9	
7	8.89	59600.0	54500.0	8.89	48100.0	46200.0	8.89209	43975.3	
8	5.00	43600.0	42700.0	5.00	34800.0	35800.0	5.00049	31760.0	
9	2.81	31500.0	33000.0	2.81	24900.0	27400.0	2.81201	22724.8	

---

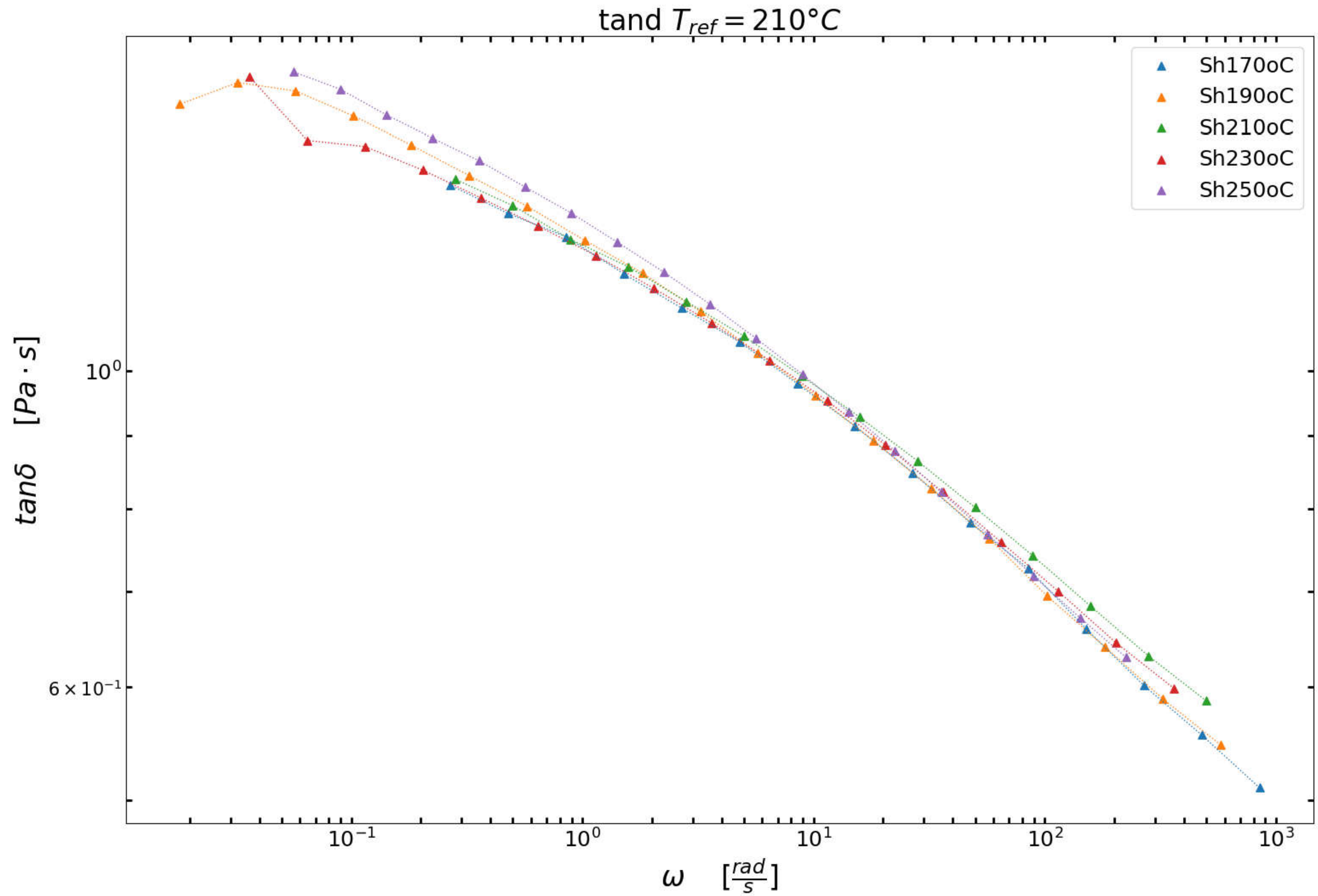
calculate WLF for each temperature and plot shifted data

master curve with $T_{ref} = 210^{\circ}C$

In [6]:
```
df_shifted = pd.read_csv("./data.csv", delimiter=",");

# Temperature of interest
T = [170, 190, 210, 230, 250];

# Reference temperature
T_0 = 210;

# k was manually tuned TTS
k = [1.7, 1.15, 1, 0.725, 0.45];
# k = [2.1, 1.3, 1, 0.9, 0.45];

# 1st empiric constant used by WLF
c_1 = 10;

for col in range(0,len(df_shifted.columns),3):
    index = int(col/3); # index with +3 increments

    # 2nd empiric constant used by WLF
    c_2 = -((c_1 * (T[index] - T_0))/(np.log10(k[index]))) - T[index] + T_0;

    # Amount of horizontal shift by WLF
    a_T = _a_T(T[index], T_0, c_1, c_2);

    # Apply a_T to the original data
    df_shifted.iloc[: , col] = df_shifted.iloc[: , col] * a_T;

# Plot and print calculated data
plot(df_shifted, 'Gs ' + r'$T_{ref} = 210 °C$', True)
plot(df_shifted, 'tand ' + r'$T_{ref} = 210 °C$', False)
print("df_shifted"); display(df_shifted.head(10));
```



Gs $T_{ref} = 210°C$
$G'(\omega)$ Sh170oC
$G''(\omega)$ Sh170oC
$G'(\omega)$ Sh190oC
$G''(\omega)$ Sh190oC
$G'(\omega)$ Sh210oC
$G''(\omega)$ Sh210oC
$G'(\omega)$ Sh230oC
$G''(\omega)$ Sh230oC
$G'(\omega)$ Sh250oC
$G''(\omega)$ Sh250oC
$G'(\omega)$ and $G''(\omega)$ $[Pa \cdot s]$
ω $[\frac{rad}{s}]$
10^3
10^4
10^5
10^{-1}
10^0
10^1
10^2
10^3


tand $T_{ref} = 210°C$
Sh170oC
Sh190oC
Sh210oC
Sh230oC
Sh250oC
10^0
6×10^{-1}
$tan\delta \quad [Pa \cdot s]$
10^{-1}
10^0
10^1
10^2
10^3
$\omega \quad [\frac{rad}{s}]$

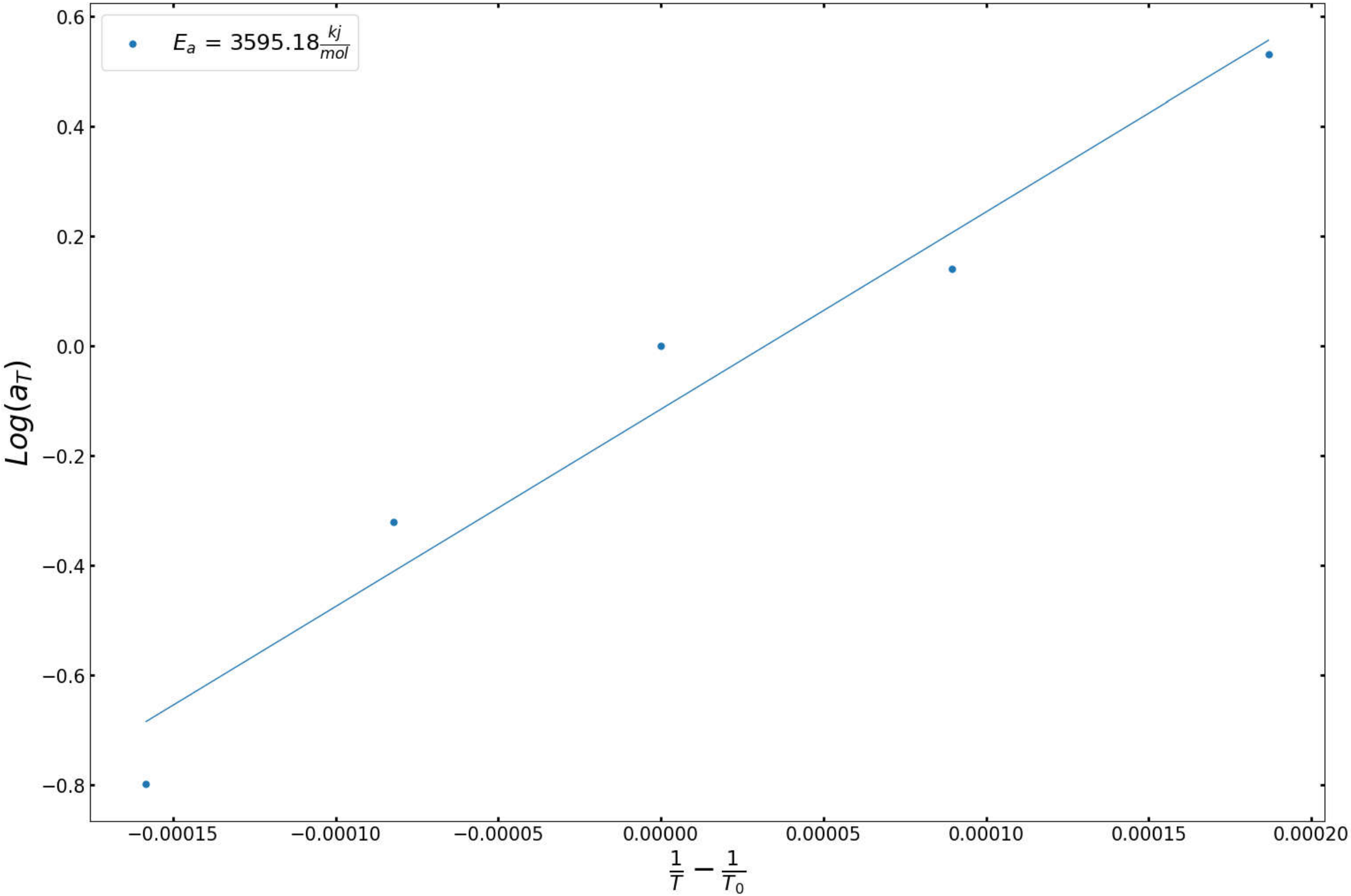
df_shifted

	frecuencia_Sh170oC	G1_Sh170oC	G2_Sh170oC	frecuencia_Sh190oC	G1_Sh190oC	G2_Sh190oC	frecuencia_Sh210oC_ref	G1_Sh210oC_ref	G2
0	850.000	343000.0	175000.0	575.0000	298000.0	163000.0	500.00000	288545.0	
1	477.700	279000.0	155000.0	323.1500	241000.0	142000.0	281.17200	231412.0	
2	268.600	226000.0	136000.0	181.7000	192000.0	123000.0	158.11700	182623.0	
3	151.130	179000.0	118000.0	102.2350	151000.0	105000.0	88.91600	141545.0	
4	85.000	139000.0	101000.0	57.5000	116000.0	88500.0	50.00200	108073.0	
5	47.770	107000.0	83700.0	32.3150	87900.0	72700.0	28.11870	81183.4	
6	26.860	80300.0	68100.0	18.1700	65500.0	58500.0	15.81250	60144.9	
7	15.113	59600.0	54500.0	10.2235	48100.0	46200.0	8.89209	43975.3	
8	8.500	43600.0	42700.0	5.7500	34800.0	35800.0	5.00049	31760.0	
9	4.777	31500.0	33000.0	3.2315	24900.0	27400.0	2.81201	22724.8	

Calculate the activation energy E_a

In [7]:
```
invTninvT0 = _invTninvT0(pd.Series(T)+273.15,T_0+273.15)

# PLOT SETUP
scale = 6;
fig   = plt.figure(figsize=(3*scale, 2*scale));
plt.rc('xtick', labelsize=15)
plt.rc('ytick', labelsize=15)
plt.tight_layout();
ax0 = plt.gca()

b = [];
x = invTninvT0;
y = np.log(k);
model = LinearRegression().fit(np.array(x).reshape((-1, 1)), np.array(y));
plt.scatter(x, y, s=25, label=r'$E_a$' + " = " + str(round(model.coef_[0], 2)) + r'$\frac{kj}{mol}$');
plt.plot(x, model.predict(np.array(x).reshape((-1, 1))), linewidth=1);

b = b + model.coef_;

ax0.tick_params(which='both', direction='in', width=2, bottom=True, top=True, left=True, right=True);

# Display plots
plt.yscale('linear');
plt.xscale('linear');
plt.xlabel(r'$\frac{1}{T} - \frac{1}{T_0}$', fontsize=24);
plt.ylabel(r'$Log(a_T)$', fontsize=24);
# plt.title(plotname, size=24);
plt.legend(prop={'size': 18});
plt.savefig('plt_' + "Capillary rheometer correction" + '.png', dpi=300, bbox_inches='tight');
display(plt);
mpl.rcParams.update(mpl.rcParamsDefault); # Recover matplotlib defaults
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\AppData\\Roaming\\Python\\Python37\\site-packages\\matplotlib\\pyplot.py'>
```



Calculate E_H

$$E_H = \frac{E_a}{R}$$

$$E_H = 432.424 \frac{kj}{mol}$$

In [8]:
```
3595.18/8.314
```

Out[8]:
```
432.42482559538126
```

Merge the data into three columns (frequency, G1, G2).

In [9]:

```python
frequency = [];
G1        = [];
G2        = [];

for col in range(0,len(df_shifted.columns),3):

    # Extract dataframe from shifted curves
    x_str  = df_shifted.columns[col];
    y1_str = df_shifted.columns[col+1];
    y2_str = df_shifted.columns[col+2];

    # Remove NANs from interesting x,y data
    df_fil = pd.DataFrame(df_shifted);
    df_fil = df_fil.dropna(subset=[x_str, y1_str, y2_str]);

    # Extract data by column
    x  = df_fil.iloc[:][x_str];
    y1 = df_fil.iloc[:][y1_str];
    y2 = df_fil.iloc[:][y2_str];

    # Place the extracted data into lists
    frequency.extend(x.tolist())
    G1.extend(y1.tolist())
    G2.extend(y2.tolist())

# Use the list to create a new dataframe with sorted values
# (combine/merge columns with similar names)
df_mc = pd.DataFrame();
df_mc['frequency'] = frequency;
df_mc['G1_'] = G1;
df_mc['G2_'] = G2;
df_mc = df_mc.sort_values('frequency');
```

Plot the viscosity curve at 205 C.

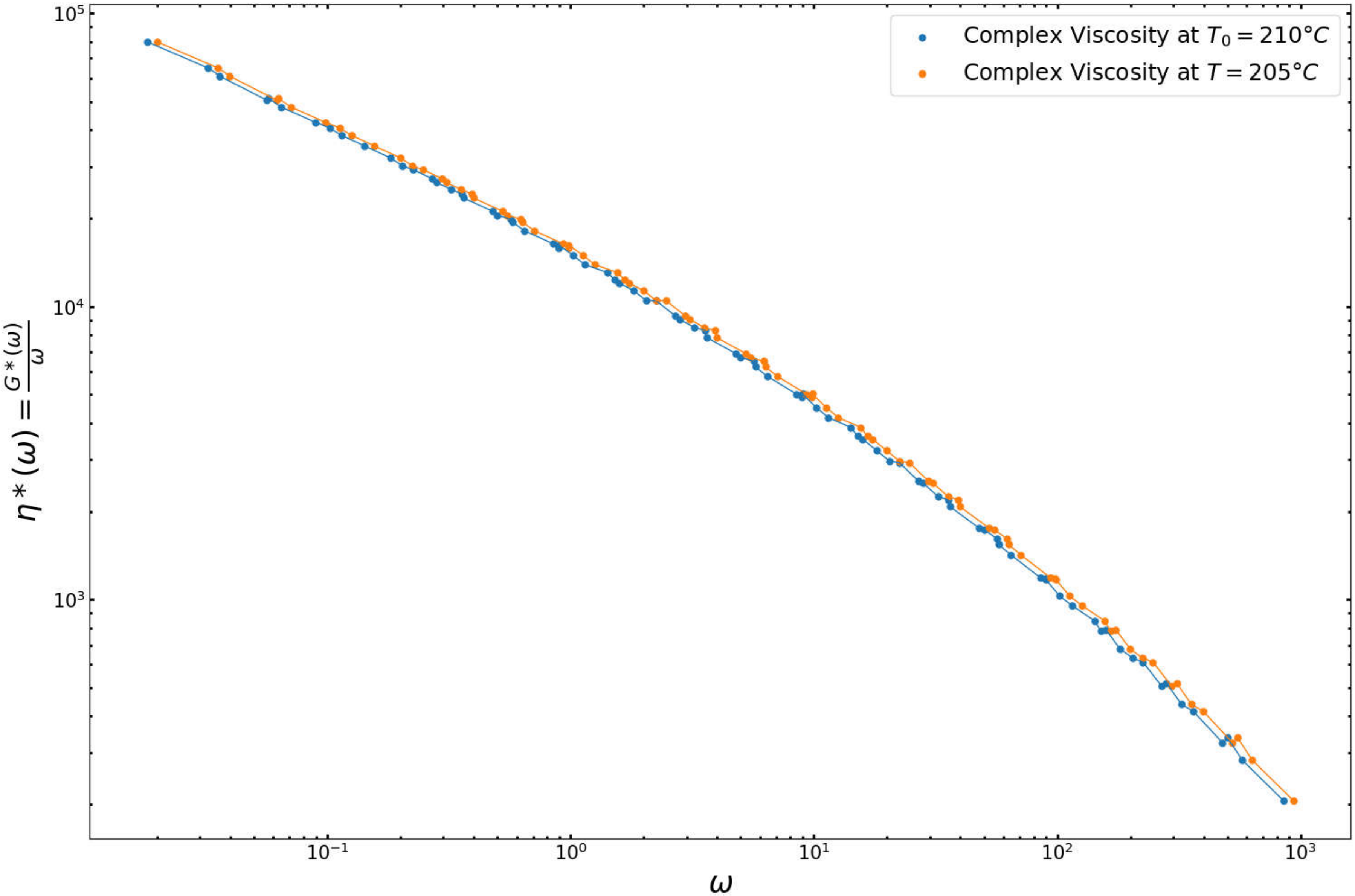
In [10]:

```
# Calculate the shifting factor to 205 C
EH = 432.424;
T  = 205;
T0 = 210;
Arrhenius = _Arrhenius(EH, T, T_0);
print(Arrhenius)
```

```
0.9988749308670454
```

In [11]:
```
# PLOT SETUP
scale = 6;
fig   = plt.figure(figsize=(3*scale, 2*scale));
plt.rc('xtick', labelsize=15)
plt.rc('ytick', labelsize=15)
plt.tight_layout();
ax0 = plt.gca()

b = [];
x = df_mc['frequency'];
y = df_mc['G2_']/df_mc['frequency'];
plt.scatter(x, y, s=25, label="Complex Viscosity at " + r'$T_0 = 210 °C$');
plt.scatter(x*(Arrhenius+0.1), y, s=25, label="Complex Viscosity at " + r'$T = 205 °C$');
plt.plot(x, y, linewidth=1);
plt.plot(x*(Arrhenius+0.1), y, linewidth=1);

ax0.tick_params(which='both', direction='in', width=2, bottom=True, top=True, left=True, right=True);

# Display plots
plt.yscale('log');
plt.xscale('log');
plt.xlabel(r'$\omega$', fontsize=24);
plt.ylabel(r'$\eta*(\omega) = \frac{G*(\omega)}{\omega}$', fontsize=24);
# plt.title(plotname, size=24);
plt.legend(prop={'size': 18});
plt.savefig('plt_' + "Capillary rheometer correction" + '.png', dpi=300, bbox_inches='tight');
display(plt);
mpl.rcParams.update(mpl.rcParamsDefault); # Recover matplotlib defaults
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\AppData\\Roaming\\Python\\Python37\\site-packages\\matplotlib\\pyplot.py'>
```



- J. Ahmed, Time–Temperature Superposition Principle and its Application to Biopolymer and Food Rheology, in: Adv. Food Rheol. Its Appl., Elsevier, 2017: pp. 209–241. https://doi.org/10.1016/B978-0-08-100431-9.00009-7 (https://doi.org/10.1016/B978-0-08-100431-9.00009-7).
- A. Oseli, A. Aulova, M. Gergesova, I. Emri, Time-Temperature Superposition in Linear and Non-linear Domain, Mater. Today Proc. 3 (2016) 1118–1123. https://doi.org/10.1016/j.matpr.2016.03.059 (https://doi.org/10.1016/j.matpr.2016.03.059).
- [1] H. Mavridis, R.N. Shroff, Temperature dependence of polyolefin melt rheology, Polym. Eng. Sci. 32 (1992) 1778–1791. https://doi.org/10.1002/pen.760322307 (https://doi.org/10.1002/pen.760322307).