Homework #3 – Solutions

Reading

- Chapter 2.5, 2.10

Problems

1. (2.14) **Hall effect and the Drude model** (Testing the Drude model)

   How good is the simple Drude model? Table 2.14 below shows the experimentally measured Hall coefficient and resistivities for various metals and their positions in the periodic table.

   a. Calculate the Hall mobility for sodium.

   b. Calculate the conduction electron concentration from the experimental value of R_H.

   c. Find how many electrons per atom are contributed to the conduction electron gas in the metal per metal atom (hint: calculate the atomic density – see Appendix C and Periodic Table).

   d. What is your conclusion? Does the Drude model work for Na?

   e. For Zn (Group IIB), $R_H = +1.04 \times 10^{-10}$ m^3 C^{-1} and $\rho = 6.01 \times 10^{-8}$ Ω m. Does the Drude model work for Zn?

Table 2.14 Measured Hall coefficients for a few metals at 25 °C

	Li	Na	K	Cs	Cu	Ag	Au	Ca	Mg	Zn	Al	In
Group	I	I	I	I	IB	IB	IB	IIA	IIA	IIB	III	III
R_H ($\times 10^{-11}$ m^3 C^{-1})	−15	−24.8	−42.8	−73.3	−5.4	−9.0	−7.2	−17.8	−8.3	+10.4	−3.4	−7.0
ρ (nΩ m)	92.8	48.8	73.9	208	17.1	16.7	22.6	33.6	44.8	60.1	27.1	83.7

Note: Data from various sources combined, including C. Hurd, *The Hall Coefficient of Metals and Alloys,* Plenum, New York, 1972.

Solution

Here, we do all the elements in Table 2.14, including Na and Zn.

Consider Li, the first element in Group I.

(a) Consider the magnitude of the conductivity product with R_H,

$$\left|\sigma R_H\right| = \left|(en\mu_d)\left(\frac{-1}{en}\right)\right| = \mu_d$$

The drift mobility μ_d here is called the Hall mobility μ_H due to the fact that it is found through the product of the Hall coefficient and conductivity.

$$\mu_H = \left|\sigma R_H\right| = \frac{\left|R_H\right|}{\rho} = \frac{15\times10^{-11}\,\text{m}^{-3}\,\text{C}^{-1}}{92.8\times10^{-9}\,\Omega\,\text{m}} = 1.62\times10^{-3}\,\text{m}^2\,\text{V}^{-1}\,\text{s}^{-1} = 16.2\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$$

(b) From the equations for R_H, we have

$$n = -\frac{1}{eR_H} = -\frac{1}{(1.602\times10^{-19}\,\text{C})(-15\times10^{-11}\,\text{m}^{-3}\,\text{C}^{-1})} = 4.161\times10^{28}\ \text{m}^{-3}.$$

(c) We can get its density and atomic mass from the Appendix at the end of the textbook. If D is the density, M_{at} is the atomic mass and N_A is Avogadro's number, then the atomic concentration n_{at} is

$$n_{\text{at}} = \frac{DN_A}{M_{\text{at}}} = \frac{(540\,\text{kg m}^{-3})(6.022\times10^{23}\,\text{mol}^{-1})}{(6.94\times10^{-3}\,\text{kg mol}^{-1})} = 4.686\times10^{28}\,\text{m}^{-3}$$

We can calculate the number of electrons per Li atom that is in the electron gas as follows

$$x = \frac{n}{n_{\text{at}}} = \frac{4.161\times10^{28}\,\text{m}^{-3}}{4.686\times10^{28}\,\text{m}^{-3}} = 0.89$$

This is close to 1, the valency of Li. The difference is only 11%. Table 2Q14-1 (next page) lists the calculations for other elements in Table 2.14.

Conclusions:

The basic idea is "How good is the simple Drude model?"

(1) Group I elements, Li, **Na**, K, Cs are very close to expected Drude model values with x close to the valency 1; x = 0.89 – 1.10

(2) Group IB, Ag, Cu, Au, have x = 1.18 – 1.47. Although there is a clear deviation from the Drude model by as much as 47%, the sign is correct and the magnitude is very roughly correct, within 47%

(3) Mg, from IIA, has a valency of 2.R_H gives x = 1.74 and the difference is only 26%, again the Drude model is not bad.

(4) **Zn is a metal and in Group IIB. The Drude model is a total failure as the sign is wrong.**

(5) Ca from Group IIA has x = 1.52. The sign is right and the magnitude is very roughly right to within 49%

(6) Group III with Al and In, we find x = 2.33 (In) – 3.05 (Al). The Drude model again is successful in predicting the sign and a rough value for the magnitude, within 67%.

(7) **The Drude model works best with Group I elemetns (Li, Na, K, Cs) and in certain cases such as Zn it totally fails.**

Table 2Q14-1 Calculations from Hall coefficient and conductivity

N_A	6E+23			q =	1.6E-19					
		g/mole	g /cm^3	1/m^3	EXPERIMENT	1/m^3			nΩ m	m^2/Vs
Valency	Metal	Mat	Density	nat	RH x 1E-11	n from RH	*x*	Difference (%)	Resistivity	Hall mobility
1	Li	6.94	0.54	4.686E+28	-15	4.161E+28	0.89	11.2	92.8	16.16
1	Na	22.99	0.968	2.536E+28	-24.8	2.517E+28	0.99	0.7	48.8	50.82
1	K	39.10	0.862	1.328E+28	-42.8	1.458E+28	1.10	-9.8	73.9	57.92
1	Cs	132.91	1.93	8.745E+27	-73.3	8.516E+27	0.97	2.6	208	35.24
1	Ag	107.87	10.49	5.856E+28	-9	6.936E+28	1.18	-18.4	16.7	53.89
1	Cu	63.55	8.96	8.491E+28	-5.4	1.156E+29	1.36	-36.1	17.1	31.58
1	Au	196.97	19.3	5.901E+28	-7.2	8.670E+28	1.47	-46.9	22.6	31.86
2	Mg	24.31	1.74	4.311E+28	-8.3	7.521E+28	1.74	25.6	44.8	18.53
2	Zn	65.38	7.13	6.567E+28	10.4	-6.002E+28	-0.91	291.4	60.1	17.30
2	Ca	40.08	1.54	2.314E+28	-17.8	3.507E+28	1.52	48.5	33.6	52.98
3	Al	26.98	2.7	6.026E+28	-3.4	1.836E+29	3.05	-4.7	27.1	12.55
3	In	114.82	7.31	3.834E+28	-7	8.917E+28	2.33	67.4	83.7	8.36

Problem 2 - (2.42) Thin films of Cu on Si (100) surface

Different thickness polycrystalline Cu films have been deposited on the (100) surface of a Si crystal. Their resistivities have been measured as summarized in Table 2.22. For these films, the average grain size d has been shown to be related to the film thickness D by d ≈ D/2.3.

a. Use Matthiessen' s rule to combine Fuch-Sondheimer and Mayadas-Shatzkes equations as in

$\rho_{film} = \rho_{crystal} + \Delta\rho_{MS} + \Delta\rho_{SF}$

where $\rho_{crystal}$ is the bulk resistivity of the Cu crystal ($\rho_{crystal}$ = 17.0 nΩ m), and $\Delta\rho_{MS}$ and $\Delta\rho_{SF}$ are the contributions to resistivity arising from the scattering of electrons at the grain boundary and surfaces respectively; that is, the Mayadas-Shatzkes and Fuch-Sondheimer contributions respectively (see textbook).

The combined resistivity is defined using the grain boundary scattering Mayadas-Shatzkes formula (Eqn. 2.72a/b in Kasap 4th Ed.) First define β, using D/2.3 for the grain diameter:

In[1]:=
```
beta = lambda / (myD / 2.3) (R / (1 - R))
```

Out[1]=
$$\frac{2.3\ \text{lambda}\ R}{\text{myD}\ (1 - R)}$$

In[2]:=
```
rhoMS = rhoCrystal ((1 - 3/2 beta + 3 beta^2 - 3 beta^3 Log[1 + 1/beta])^-1 - 1)
```

Out[2]=
$$\text{rhoCrystal}\left(-1 + \frac{1}{1 - \frac{3.45\ \text{lambda}\ R}{\text{myD}\ (1-R)} + \frac{15.87\ \text{lambda}^2\ R^2}{\text{myD}^2\ (1-R)^2} - \frac{36.501\ \text{lambda}^3\ R^3\ \text{Log}\left[1+\frac{0.434783\ \text{myD}\ (1-R)}{\text{lambda}\ R}\right]}{\text{myD}^3\ (1-R)^3}}\right)$$

Note, the - 1 term was added to Eqn. 2.72a since that equation is for the total resistivity (including grain boundary scattering and the crystal). We want to pull out the crystal term separately to use the Matthiessen form above.

From Eqn. 2.76 (Kasap 4th Ed.), we again leave out the crystal term (remove the +1) to have

In[3]:=
```
rhoSF = rhoCrystal (3 lambda / (8 myD) (1 - p))
```

Out[3]=
$$\frac{3\ \text{lambda}\ (1 - p)\ \text{rhoCrystal}}{8\ \text{myD}}$$

Putting these together, we have

In[4]:=
```
Framed[rhoFilm = rhoCrystal + rhoMS + rhoSF]
```

Out[4]=
$$\text{rhoCrystal} + \frac{3\,\text{lambda}\,(1-\text{p})\,\text{rhoCrystal}}{8\,\text{myD}} + \text{rhoCrystal}\left(-1 + \frac{1}{1 - \frac{3.45\,\text{lambda R}}{\text{myD}\,(1-\text{R})} + \frac{15.87\,\text{lambda}^2\,\text{R}^2}{\text{myD}^2\,(1-\text{R})^2} - \frac{36.501\,\text{lambda}^3\,\text{R}^3\,\text{Log}\left[1+\frac{0.434783\,\text{myD}\,(1-\text{R})}{\text{lambda R}}\right]}{\text{myD}^3\,(1-\text{R})^3}}\right)$$

b. Plot the experimental data. ρ against $1/D$ and also ρ against D as a log-log plot in *Mathematica*.

We can create two lists. It's a little cumbersome, but more flexible for data manipulation.

In[5]:=
```
ExptD = {407, 222, 170, 120, 101, 85.4, 68.5, 51.2, 34.1, 17.2, 8.59}
```

Out[5]=
```
{407, 222, 170, 120, 101, 85.4, 68.5, 51.2, 34.1, 17.2, 8.59}
```

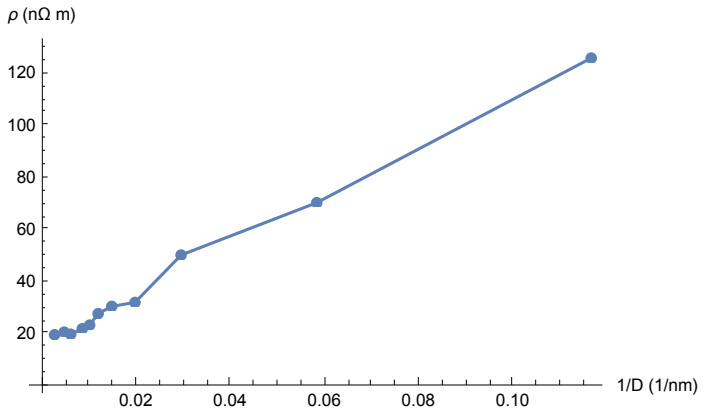
In[6]:=
```
Exptrho = {19.8, 20.8, 20., 22.1, 23.5, 27.9, 30.7, 32.2, 50.4, 70.5, 126}
```

Out[6]=
```
{19.8, 20.8, 20., 22.1, 23.5, 27.9, 30.7, 32.2, 50.4, 70.5, 126}
```

Note, since we created two separate lists, we have to create a {x, y} array for ListPlot, which we can do with the Table function.

In[7]:=
```
ListPlot[Table[{1 / ExptD[[n]], Exptrho[[n]]}, {n, Length[ExptD]}], Joined → True,
 PlotMarkers → Automatic, AxesLabel → {"1/D (1/nm)", "ρ (nΩ m)"}]
```

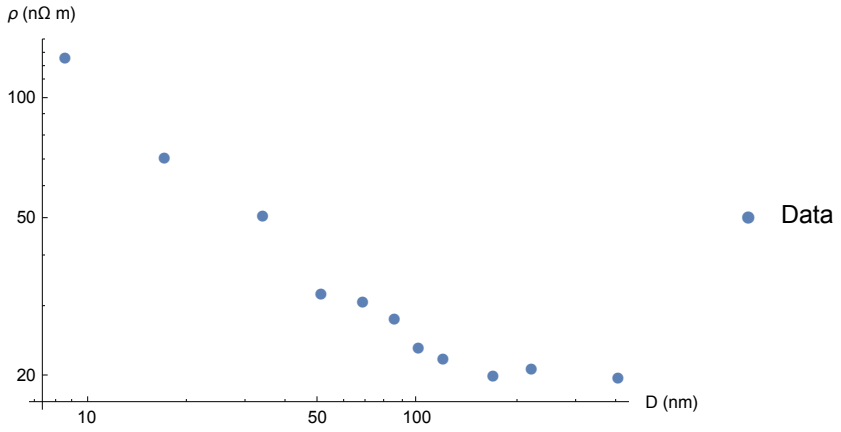
Out[7]=



The linear shape of the experimental resistivities plotted versus inverse film thickness is consistent with surface scattering as described by the Fuchs-Sondheimer equation (Eqn. 2.76).

In[8]:=
```
ExptDataPlot =
 ListLogLogPlot[Legended[Table[{ExptD[[n]], Exptrho[[n]]}, {n, Length[ExptD]}], "Data"],
  PlotMarkers → "●", AxesLabel → {"D (nm)", "ρ (nΩ m)"}]
```

Out[8]=



It is difficult to predict the expected form for the plot above, but we can use our function to compare with our combined resistivity equation, which accounts for both surface and grain boundary scattering.

c. In a new plot, add a plot of the calculated ρ (from part (a)) in the ρ vs. D graph by taking $p = 0$, $\lambda = 40$ nm, and $R = 0.25$. Try a slightly greater and slightly lower R values (e.g., 0.20 and 0.30) to see how the predicted curve changes with respected to the data. What is your conclusion?

In[9]:=
```
lambda = 40;
```

In[10]:=
```
rhoCrystal = 17.0;
```

Let' s check that our film resistivity formula works.

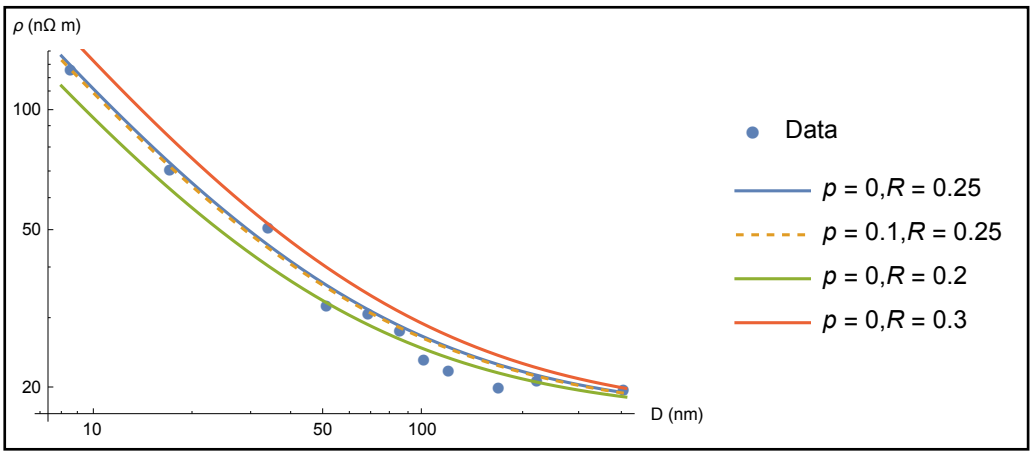
In[11]:=
```
rhoFilm /. {myD → 10, R → 0.5, p → 0.2}
```

Out[11]=
```
247.005
```

Ok, now we use the Show function to combine all of the plot. This looks complicated, but it was built in parts and much of it is copy/paste.

In[12]:=
```
Framed[Show[ExptDataPlot, LogLogPlot[{
    Legended[rhoFilm /. {R → 0.25, p → 0.0}, "p = 0,R = 0.25"],
    Legended[rhoFilm /. {R → 0.25, p → 0.1}, "p = 0.1,R = 0.25"],
    Legended[rhoFilm /. {R → 0.2, p → 0.0}, "p = 0,R = 0.2"],
    Legended[rhoFilm /. {R → 0.3, p → 0.0}, "p = 0,R = 0.3"]
  }, {myD, 8, 410}, PlotStyle → {Solid, Dashed, Solid, Solid}]]]
```

Out[12]=

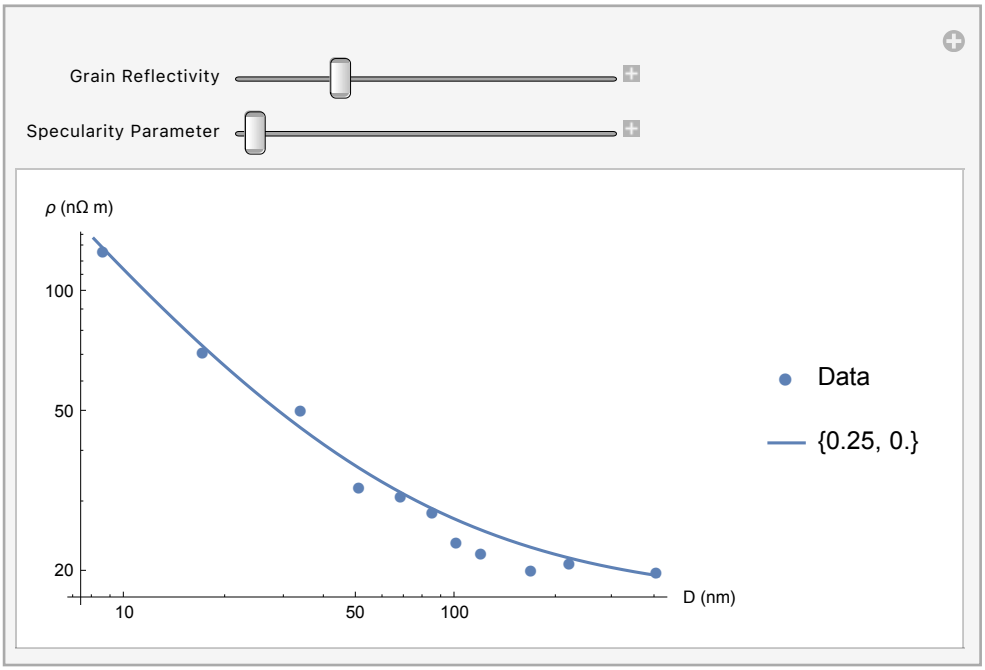


Based on the above plot, the data seem fairly well described by the combined film resistivity model. The value of 0.25 for *R* seems good, but *R* of 0.2 is close to some of the data. *R* of 0.3 seems too high. The value of *p* seems to change the curve only slightly.

In general, the data are well described by *a* model of film resistivity that includes both grain boundary scattering with *a* 0.25 probability of reflection from *a* grain boundary and very diffusive surface scattering (low value of specularity parameter, *p*).

In[13]:=
```
Manipulate[Show[ExptDataPlot,
  LogLogPlot[Legended[rhoFilm /. {R → S, p → q}, {S, q}], {myD, 8, 410}]],
 {{S, 0.25, "Grain Reflectivity"}, 0, 1}, {{q, 0.0, "Specularity Parameter"}, 0, 1}]
```

Out[13]=



With Manipulate, still had to substitute the Manipulate parameters in for the values of *p* and *R*. After adjusting the parameters, the data seem well described by very specular surfaces. From this data set, it may be difficult to find a unique solution to the film resistivity. We may need more information about the film properties (e.g., surface roughness, void fraction, etc.).

In[14]:=
```
filmdata = Table[{ExptD[[n]], Exptrho[[n]]}, {n, Length[ExptD]}];
```

In[15]:=
```
rhoFilm
```

Out[15]=
$$17. + \frac{255. \times (1-p)}{myD} + 17. \times \left(-1 + \frac{1}{1 - \frac{138.\,R}{myD\,(1-R)} + \frac{25\,392.\,R^2}{myD^2\,(1-R)^2} - \frac{2.33606\times 10^6\,R^3\,\text{Log}\left[1+\frac{0.0108696\,myD\,(1-R)}{R}\right]}{myD^3\,(1-R)^3}} \right)$$

In[16]:=
```
nlmf = NonlinearModelFit[filmdata, {rhoFilm, {0 ≤ R ≤ 1, 0 ≤ p ≤ 1}}, {R, p}, myD]
```

Out[16]=
$$\text{FittedModel}\left[17. + \frac{254.996}{myD} + 17. \times \left(-1 + \frac{1}{1 + \frac{2612.84}{myD^2} - \frac{\ll 18 \gg}{myD} - \frac{77109.5\,\text{Log}[1+0.0338848\,myD]}{myD^3}} \right) \right]$$

In[17]:=
```
nlmf["AdjustedRSquared"]
```

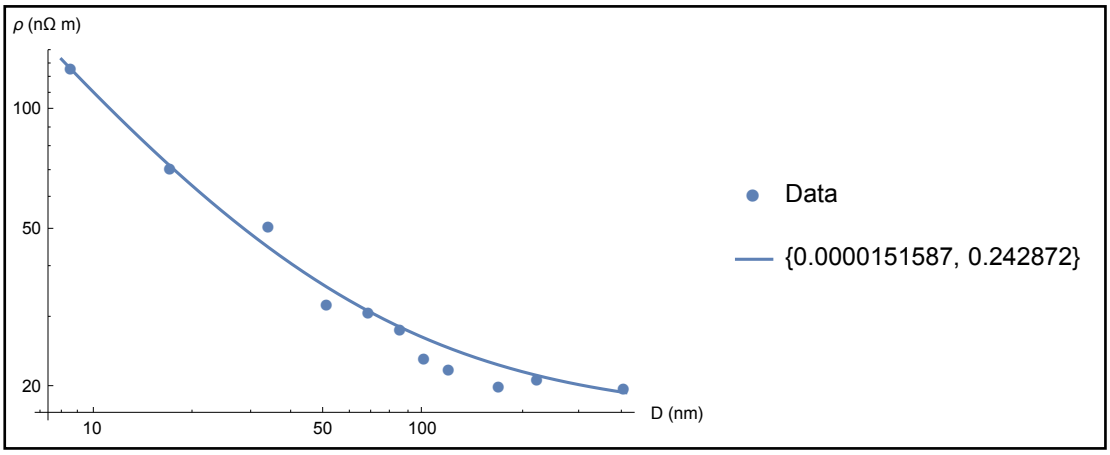
Out[17]=
```
0.996929
```

In[18]:=
```
{Rfit, pfit} = Values[nlmf["BestFitParameters"]]
```

Out[18]=
```
{0.242872, 0.0000151587}
```

In[19]:=
```
Framed[Show[ExptDataPlot, LogLogPlot[
    Legended[rhoFilm /. {R → Rfit, p → pfit}, {pfit, Rfit}], {myD, 8, 410}]]]
```

Out[19]=



The above plot shows the model with the fitted parameters, which matches the data closely. The adjusted R^2value of 0.997 indicates a high quality of fit (R^2 is 1 for a perfect fit).