Statistical Thermodynamics First Homework Assignment

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The isothermal electrical susceptibility χ_T *of an oil is governed by the relationship*

$$\frac{\chi}{\chi+3} \propto 1 + \frac{C}{T}$$

where $C = 30\,\mathrm{K}$. *In an electric field of* $10^7\,\mathrm{Vm}$ *at* $27\,^{\circ}\mathrm{C}$, *the oil has density* $800\,\mathrm{kg/m^3}$, $\chi_T = 2$, *and specific heat capacity at constant polarization* $c_P = 1700\,\mathrm{J/kgK}$. *Assuming the volume of the oil is constant, find the difference in specific heat capacities at constant electric field and constant polarization* $c_E - c_P$ *and the difference in isothermal and isentropic susceptibilities* $\chi_T - \chi_S$.

Finding Difference in Heat Capacities

We recognize that we are working with a (E, P, T) system, where electric field magnitude E is the intensive variable, electric polarization P is the extensive variable, and T is temperature. Work is given by the product $\delta W = VE\,\mathrm{d}P$, where the volume factor V is necessary to give units of joules for work.

Useful Identities for a (E, P, T) System

For such a system, some useful identities are:

$$\mathrm{d}F = -S\,\mathrm{d}T + VE\,\mathrm{d}P$$

$$\mathrm{d}G = -S\,\mathrm{d}T - VP\,\mathrm{d}E$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\left(\frac{\partial E}{\partial T}\right)_P \tag{1}$$

$$\left(\frac{\partial S}{\partial E}\right)_T = -V\left(\frac{\partial P}{\partial T}\right)_E \tag{2}$$

$$c_E = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_E \tag{3}$$

$$c_P = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_P \tag{4}$$

Expression for Difference of Heat Capacities

For such a system, entropy is given by $S = S(T,P) = S(T,P(T,E))$. The partial derivative of entropy with respect to T at constant E, found with the chain rule, is:

$$\left(\frac{\partial S}{\partial T}\right)_E = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_E \tag{5}$$

Recognizing the expression for c_E from Equation 3 in the left side of Equation 5, we write:

$$c_E = \frac{T}{m}\left[\left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_E\right]$$

Referring to Equation 4, we identify the first term as

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{m}{T}c_P$$

Rearranging yields an expression for the desired quantity $c_E - c_P$.

$$c_E - c_P = \frac{T}{m}\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_E \tag{6}$$

To find the desired difference in heat capacities, we must determine the unknown quantities

$$\left(\frac{\partial S}{\partial P}\right)_T \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)_E$$

Equations of State

General Electric Equation of State

For a general electric substance:

$$P = \epsilon_0 \chi E \tag{7}$$

where $\chi = \chi(T)$ is the temperature-dependent electric susceptibility. We will use this equation to find two partial derivatives that we will need for our analysis. First, the partial derivative of Equation 7 with respect to T at constant E is

$$\left(\frac{\partial P}{\partial T}\right)_E = \epsilon_0 E \left(\frac{\partial \chi}{\partial T}\right)_E \tag{8}$$

Second, the partial derivative of Equation 7 with respect to T at constant P, found with the product rule, gives:

$$0 = \epsilon_0\left[E\left(\frac{\partial \chi}{\partial T}\right)_P + \chi\left(\frac{\partial E}{\partial T}\right)_P\right] \qquad / : \epsilon_0\chi$$

$$\left(\frac{\partial E}{\partial T}\right)_P = -\frac{E}{\chi}\left(\frac{\partial \chi}{\partial T}\right)_P \tag{9}$$

Principle Equation of State

For our case in particular, we are given the equation of state

$$\frac{\chi}{\chi+3} \propto \left(1+\frac{C}{T}\right)$$

Writing $\chi = \chi(T)$, we proceed as follows:

$$\begin{aligned}
&\frac{\chi}{\chi+3} = k\left(1+\frac{C}{T}\right) && /\ln \\
&\ln\left(\frac{\chi}{\chi+3}\right) = \ln\left[k\left(1+\frac{C}{T}\right)\right] \\
&\ln\chi - \ln(\chi+3) = \ln k + \ln\left(1+\frac{C}{T}\right) && /\left(\frac{\partial}{\partial T}\right)_E \\
&\left(\frac{\partial\chi}{\partial T}\right)_E\left(\frac{1}{\chi}-\frac{1}{\chi+3}\right) = -\frac{C}{T^2}\frac{1}{1+\frac{C}{T}} \\
&\left(\frac{\partial\chi}{\partial T}\right)_E\frac{3}{\chi(\chi+3)} = \frac{C}{T(T+C)}
\end{aligned}$$

Giving the final result

$$\left(\frac{\partial\chi}{\partial T}\right)_E = \frac{C}{3}\frac{\chi(\chi+3)}{T(T+C)} \tag{10}$$

An analogous derivation shows that

$$\left(\frac{\partial\chi}{\partial T}\right)_P = \frac{C}{3}\frac{\chi(\chi+3)}{T(T+C)} \tag{11}$$

Finding Unknown Partial Derivatives

We must find two unknown partial derivatives to solve for the difference in specific heat capacities in Equation 6.

Finding the First Unknown Derivative

Referring in turn to Maxwell's first relation (Equation 1), Equation 9, and finally Equation 11 we see that:

$$\begin{aligned}
\left(\frac{\partial S}{\partial P}\right)_T = -V\left(\frac{\partial E}{\partial T}\right)_P &= \frac{m}{\rho}\frac{E}{\chi}\left(\frac{\partial\chi}{\partial T}\right)_P \\
&= \frac{mE}{\rho\chi}\frac{C}{3}\frac{\chi(\chi+3)}{T(T+C)}
\end{aligned}$$

where we have used the relationship $V = \frac{m}{\rho}$.

Finding the Second Unknown Derivative

Referring in turn to Equation 8 and Equation 10 gives:

$$\left(\frac{\partial P}{\partial T}\right)_E = \epsilon_0 E\left(\frac{\partial\chi}{\partial T}\right)_E = \epsilon_0 E\frac{C}{3}\frac{\chi(\chi+3)}{T(T+C)}$$

Finding Difference of Heat Capacities

Plugging the two unknown partial derivatives into Equation 6 gives

$$\begin{aligned}
c_E - c_P &= \frac{T}{m}\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_E \\
&= \frac{T}{m}\frac{mE}{\rho\chi}\frac{C}{3}\frac{\chi(\chi+3)}{T(T+C)}\epsilon_0 E\frac{C}{3}\frac{\chi(\chi+3)}{T(T+C)} \\
&= \epsilon_0\frac{E^2}{9\rho}\frac{C^2\chi(\chi+3)^2}{T(T+C)^2} \\
&= 8.85\times 10^{-12}\,\mathrm{C}\cdot\mathrm{V}^{-1}\cdot\mathrm{m}^{-1}\frac{\left(10^7\,\mathrm{V}\cdot\mathrm{m}^{-1}\right)^2}{9\cdot 800\,\mathrm{kgm}^{-3}}\frac{(30\,\mathrm{K})^2\cdot 2\cdot(2+3)^2}{300\,\mathrm{K}\cdot(300\,\mathrm{K}+30\,\mathrm{K})^2} \\
&= 1.69\times 10^{-4}\,\frac{\mathrm{C}\cdot\mathrm{V}}{\mathrm{kg}\cdot\mathrm{K}} \\
&= 1.69\times 10^{-4}\,\frac{\mathrm{J}}{\mathrm{kg}\cdot\mathrm{K}}
\end{aligned}$$

Finding Difference in Susceptibilities

This problem can be solved quite quickly by respecting the fact that for a general (X, Y, T) thermodynamic system, where X is the intensive variable and Y is the extensive variable, the ratio of isothermal and isentropic susceptibilities $\frac{\chi_T}{\chi_S}$ equals the ratio of intensive and extensive heat capacities $\frac{c_X}{c_Y}$. In our case:

$$\frac{c_E}{c_P} = \frac{\chi_T}{\chi_S}$$

Writing $\Delta c = c_E - c_P$ and $\Delta\chi = \chi_T - \chi_S$, we get

$$\begin{aligned}
\frac{c_P+\Delta c}{c_P} &= \frac{\chi_T}{\chi_T - \Delta\chi} \\
\chi_T - \Delta\chi &= \frac{\chi_T c_P}{c_P + \Delta c} \\
\Delta\chi = \chi_T - \chi_T\left(\frac{c_P}{c_P+\Delta c}\right) &= \chi_T\left(1 - \frac{c_P}{c_P+\Delta c}\right) \\
&= 2\left(1 - \frac{1700\,\frac{\mathrm{J}}{\mathrm{kg\,K}}}{1700\,\frac{\mathrm{J}}{\mathrm{kg\,K}} + 1.69\times 10^{-4}\,\frac{\mathrm{J}}{\mathrm{kg\,K}}}\right) \\
&= 2\left(1 - \frac{1700}{1700.000169}\right) \\
&= 1.99\times 10^{-7}
\end{aligned}$$