1. Use the Debye approximation to find the following thermodynamic functions of a solid as a function of $T$.

(a) $\ln(Z)$

(b) The mean energy

(c) The entropy

Express your answers in terms of the function $D(y) = \frac{3}{y^3} \int_0^y \frac{x^3 dx}{e^x - 1}$

**Solution:**

(a) 

$$\ln Z = \beta N\eta - \int_0^\infty \ln(1 - e^{-\beta \hbar \omega})\sigma_D(\omega) d\omega$$

where $\sigma_D(\omega) = \frac{3V}{\pi^2 \omega^2}$ for $\omega < \omega_D$ and 0 for $\omega > \omega_D$. Since $V = \frac{6\pi^2 N (c/\omega_D)^3}{2}$ we find

$$\ln Z = \beta N\eta - \frac{9N}{\omega_D^3} \int_0^{\omega_D} \ln(1 - e^{-\beta \hbar \omega})\omega^2 d\omega$$

In terms of dimensionless variables $x = \beta \hbar \omega$ and $y = \beta \hbar \omega_D$ we get

$$\ln Z = \frac{y N\eta}{\hbar \omega_D} \frac{9N}{y^3} \int_0^y \ln(1 - e^{-x})x^2 dx = \frac{y N\eta}{\hbar \omega_D} \frac{9N}{y^3} \left[ \frac{\ln(1 - e^{-x})x^3}{3} \right]_0^y - \frac{1}{3} \int_0^y \frac{x^3 dx}{e^x - 1}$$

(b) The mean energy is

$${\cal E} = -\frac{\partial}{\partial \beta} \ln Z = -\hbar \omega_D \frac{\partial}{\partial y} \ln Z = -N\eta + \frac{3N\hbar \omega_D e^{-y}}{1 - e^{-y}} + \frac{9N\hbar \omega_D}{y^4} \int_0^y \frac{x^3 dx}{e^x - 1} - \frac{3N\hbar \omega_D}{y^3} \frac{y^3}{e^y - 1} \Rightarrow$$

$${\cal E} = -N\eta + \frac{3N}{\beta} D(y) = -N\eta + 3NkT \frac{D(\theta_D/T)}{T}$$

(c) 

$$S = k(\ln Z + \beta E) = Nk[-3\ln(1 - e^{-y}) + 4D(y)] = Nk[-3\ln(1 - e^{-\theta_D/T}) + 4D(\theta_D/T)]$$

2. Evaluate $D(y)$ in the two limits and use this to calculate the quantities of the previous problem.

**Solution:**

For $y \gg 1$ the upper limit in the integral can be taken to infinity, so

$$D(y) = \frac{3}{y^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{5y^3}$$

For $y \ll 1$ we expand $e^x \approx 1 + x$ so

$$D(y) = \frac{3}{y^3} \int_0^\eta x^2 dx = 1$$
For the temperature much smaller than the Debye temperature, we get

\[ \ln Z = \frac{N\eta}{kT} + \frac{N\pi^4 T^3}{5\theta_D^3} \]

\[ E = -N\eta + \frac{3\pi^4 NkT^4}{5\theta_D^3} \]

\[ S = \frac{4\pi^4}{5} Nk(\frac{T}{\theta_D})^3 \]

For the temperature much greater than the Debye temperature, we find using \( e^y \approx 1 + y \)

\[ \ln Z = \frac{N\eta}{kT} - 3N \ln\theta_D/T + N \]

\[ E = -N\eta + 3NkT \]

\[ S = Nk[-3\ln\theta_D/T + 4] \]

3. The expression for the energy of a solid depends in general on the volume. Use the Debye approximation to find the equation of state of the solid, i.e. find the pressure as a function of \( V \) and \( T \). What are the limiting cases when \( T \ll \Theta_D \) and \( T \gg \Theta_D \). Express your answer in terms of the quantity \( \gamma = -\frac{V}{\Theta_D^4} \frac{d\theta_D}{dV} \)

**Solution:**

\[ p = \frac{1}{\beta} \frac{\partial}{\partial V} \]

\[ \ln Z = N \frac{\partial \eta}{\partial V} + 3NkTe^{-\theta_D/T} \left( -\frac{1}{T} \frac{\partial \theta_D}{\partial V} \right) + NkT \left( \frac{\partial D(\theta_D/T)}{\partial (\theta_D/T)} \right) \left( \frac{d(\theta_D/T)}{dV} \right) \]

where

\[ \left[ \frac{\partial D(\theta_D/T)}{\partial (\theta_D/T)} \right] = -\frac{9}{(\Theta_D/T)^4} \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} + \frac{3}{e^{\Theta_D/T} - 1} \]

\[ p = N \frac{\partial \eta}{\partial V} - \frac{3NkT}{\theta_D} D(\theta_D/T) \frac{d\theta_D}{dT} \]

In terms of \( \gamma \) this becomes

\[ p = N \frac{\partial \eta}{\partial V} - \frac{3N\gamma kT}{V} D(\theta_D/T) \]

For small \( T \)

\[ p = N \frac{\partial \eta}{\partial V} + \frac{3\pi^4 \gamma NkT^4}{5V\theta_D^4} \]

For high \( T \)

\[ p = N \frac{\partial \eta}{\partial V} + \frac{3\gamma NkT}{V} \]
4. Assume that \( \gamma \) is independent of temperature. Show that the coefficient of thermal expansion \( \alpha \) is then related to \( \gamma \) by the relation

\[
\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p = \kappa \frac{\partial p}{\partial T} V = \kappa \gamma \frac{C_V}{V}
\]

where \( \kappa \) is the compressibility

Solution:

\[
p = N \frac{\partial \eta}{\partial V} + \gamma \frac{E + N \eta}{V}
\]

Thus

\[
\alpha = \kappa \left( \frac{\partial p}{\partial T} \right)_V = \kappa \gamma \left( \frac{\partial E}{\partial T} \right)_V = \kappa \gamma \frac{C_V}{V}
\]