Q4 Consider a simple model of a solid of volume V that contains a fixed number N of atoms. There are two contributions to its internal energy U. The first, U_{bonds}, is the potential energy of the chemical bonds and is a function of V but not of the temperature T. The second, U_{phonons}, depends on both V and T. The total internal energy U is $U = U_{\text{bonds}} + U_{\text{phonons}}$. Similarly the total pressure is given by $P = P_{\text{bonds}} + P_{\text{phonons}}$. The phonon modes are modeled as a set of $3N$ quantum harmonic oscillators whose angular frequencies ω_n ($n = 1, 2, \ldots, 3N$) depend on V. Assume that the parameter

$$\gamma \stackrel{\text{def}}{=} -\frac{V}{\omega_n}\frac{\partial \omega_n}{\partial V}$$

that determines the frequency variation with volume is *same* for all phonon modes, and is positive. The solid's elastic bulk modulus κ, its coefficient of volume thermal expansion α, and its specific heat at constant volume C_V, are defined by

$$\kappa = -V\left(\frac{\partial P}{\partial V}\right)_T, \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

a) Write down the partition function for the $3N$ quantum harmonic oscillators, and hence find the phonon contribution F_{phonon} to the Helmholtz free energy for the solid. Use

$$dF_{\text{phonon}} = -S_{\text{phonon}}dT - P_{\text{phonon}}dV$$

to show that the pressure exerted by the phonons P_{phonon} is proportional to U_{phonon} and find the constant of proportionality in terms of γ and V.

b) Use the Gibbs free energy $G = U - TS + PV$ to deduce a Maxwell relation between $(\partial V/\partial T)_P$ and $(\partial S/\partial V)_T$. Hence or otherwise deduce that the product $\alpha\kappa$ can be expressed in terms of $(\partial S/\partial V)_T$.

c) Only the phonons contribute to the entropy, and the total entropy is simply the sum of the entropies of the individual oscillator modes. Show that each phonon mode's contribution to the entropy S is a function only of ω_n/T. Deduce that $(\partial S/\partial V)$ is proportional to C_V, and find the constant of proportionality in terms of γ and other quantities.

d) Combine your results from parts (b) and (c) to find an expression for the coefficient of thermal expansion α in terms of γ, C_V, κ and V.