

Physics 460/560 Lecture 8

• Thermal expansion of a crystal

Solids normally expand with increasing temperature. We will see that anharmonic effects are necessary to describe this effect.

To investigate thermal expansion,

we must determine the equation

• of state $P = P(T, V)$ of the crystal. We use the relation

$$P = - \left. \frac{\partial F}{\partial V} \right|_T ,$$

where

$$F = -k_B T \ln Z$$

is the Helmholtz free energy.

If the temperature is not too high,

• we may invoke the assumption of

Small oscillations of the atoms or ions about their equilibrium positions. The quantum energy levels of the system are

$$E(\{n_{\vec{k}s}\}) = U_0 + \sum_{\vec{k}s} \hbar \omega_{\vec{k}s} \left(n_{\vec{k}s} + \frac{1}{2} \right).$$

The partition function is a sum over all these energy levels:

$$Z = e^{-\beta E_0} \prod_{\vec{k}s} \sum_{n_{\vec{k}s}=0}^{\infty} \left(e^{-\beta \hbar \omega_{\vec{k}s}} \right)^{n_{\vec{k}s}}$$

$$= e^{-\beta E_0} \prod_{\vec{k}s} \frac{1}{1 - e^{-\beta \hbar \omega_{\vec{k}s}}}$$

$$F = -k_B T \ln Z$$

$$= E_0 + k_B T \sum_{\vec{k}s} \ln \left(1 - e^{-\beta \hbar \omega_{\vec{k}s}} \right)$$

$$P = - \left. \frac{\partial F}{\partial V} \right|_T = - \frac{\partial E_0}{\partial V} - \sum_{ks} \left(\frac{\partial \hbar \omega_{ks}}{\partial V} \right) \frac{1}{e^{\beta \hbar \omega_{ks}} - 1}$$

Thus, any temperature dependence of P comes through the volume dependence of the phonon frequencies

Experimentally, what is often measured is the change in volume with temperature at constant pressure, $\left. \frac{\partial V}{\partial T} \right|_P$. The equation of state can be expressed

$$V = V(T, P).$$

$$dV = \left. \frac{\partial V}{\partial T} \right|_P dT + \left. \frac{\partial V}{\partial P} \right|_T dP.$$

For a process at constant volume, we have

$$0 = \left. \frac{\partial V}{\partial T} \right|_p dT + \left. \frac{\partial V}{\partial p} \right|_T dp$$

or $\left. \frac{\partial p}{\partial T} \right|_V \left. \frac{\partial V}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p$

whence

$$\left. \frac{\partial V}{\partial T} \right|_p = - \frac{\left. \frac{\partial V}{\partial T} \right|_V \left. \frac{\partial p}{\partial V} \right|_T}{\left. \frac{\partial p}{\partial V} \right|_T}$$

The coefficient of thermal expansion is defined by

$$\alpha = \frac{1}{L} \left. \frac{\partial L}{\partial T} \right|_p = \frac{1}{3V} \left. \frac{\partial V}{\partial T} \right|_p$$

where L is a linear dimension of

the crystal), and the second equality assumes a crystal symmetric enough that all the linear dimensions scale in the same way with temperature. [Crystals of noncubic symmetry have direction dependent expansion coefficients.]

The previous identity implies

$$\alpha = \frac{1}{3} \frac{\frac{\partial P}{\partial T} |_{V}}{-V \frac{\partial P}{\partial V} |_{T}} = \frac{1}{3B} \frac{\partial P}{\partial T} |_{V}$$

The bulk modulus is defined by

$$B = -V \frac{\partial P}{\partial V} |_{T} .$$

Using our equation of state for a crystal, we have

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$$\alpha = \frac{1}{3B} \sum_{\vec{k}s} \left(-\frac{\partial}{\partial V} \hbar \omega_{\vec{k}s} \right) \frac{\partial \langle n_{\vec{k}s} \rangle}{\partial T}$$

The specific heat per unit volume, on the other hand, is

$$C_V = \frac{1}{V} \left. \frac{\partial E}{\partial T} \right|_V = \sum_{\vec{k}s} \frac{\hbar \omega_{\vec{k}s}}{V} \frac{\partial \langle n_{\vec{k}s} \rangle}{\partial T}$$

Thus we may write

$$\alpha = \frac{\gamma C_V}{3B},$$

where the Grüneisen parameter

γ is defined as follows

$$\gamma = \frac{\sum_{\vec{k}s} \left(-\frac{\partial \ln \omega_{\vec{k}s}}{\partial \ln V} \right) \frac{\hbar \omega_{\vec{k}s}}{V} \frac{\partial \langle n_{\vec{k}s} \rangle}{\partial T}}{\sum_{\vec{k}s} \frac{\hbar \omega_{\vec{k}s}}{V} \frac{\partial \langle n_{\vec{k}s} \rangle}{\partial T}}$$

In the case where the logarithmic derivative of $\omega_{\vec{k}s}$ with respect to volume is independent of the mode $\vec{k}s$, γ becomes simply

$$\gamma = - \frac{\partial \ln \omega}{\partial \ln V}$$

For example, in the Debye model, one has

$$\gamma_D = - \frac{\partial \ln \omega_D}{\partial \ln V}$$

- Vanishing of γ in the
- Harmonic approximation

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If the potential energy of a crystal were given exactly by

$$U = U_0 + \frac{1}{2} \sum_{\vec{R}\vec{R}'} \vec{x}(\vec{R}) \cdot \vec{C}(\vec{R}-\vec{R}') \cdot \vec{x}(\vec{R}')$$

rather than only approximately, as we have assumed, the γ would vanish! To see this, consider a crystal for which a uniform isotropic expansion (or contraction) yields a new equilibrium configuration. This is true, e.g. for cubic crystals, diamond structure, hcp, etc., but not for orthorhombic and less symmetric

crystals. However, the argument can readily be extended to less symmetric cases. Then the new equilibrium positions of the atoms/ions after increasing the volume by the factor $(1+\epsilon)^3$ would be

$$\bar{\mathbf{r}} = (1+\epsilon)\bar{\mathbf{r}}.$$

The deviations $\bar{\mathbf{x}}(\bar{\mathbf{r}})$ of the atoms/ions away from their new equilibrium positions can also be considered as deviations from the original equilibrium:

$$\bar{\mathbf{x}}(\bar{\mathbf{r}}) = \epsilon\bar{\mathbf{r}} + \bar{\mathbf{x}}(\bar{\mathbf{r}}). \quad \text{Thus}$$

$$U = U_0 + \frac{\epsilon^2}{2} \sum_{\bar{\mathbf{r}}\bar{\mathbf{r}}'} \bar{\mathbf{r}} \bar{\mathbf{C}} (\bar{\mathbf{r}} - \bar{\mathbf{r}}') \bar{\mathbf{r}}' + \frac{1}{2} \sum_{\bar{\mathbf{r}}\bar{\mathbf{r}}'} \bar{\mathbf{x}}(\bar{\mathbf{r}}) \bar{\mathbf{C}} (\bar{\mathbf{r}} - \bar{\mathbf{r}}') \bar{\mathbf{x}}(\bar{\mathbf{r}}').$$

The linear terms vanish

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Since \bar{R} is assumed to be a new equilibrium. Thus the interaction matrix

$C_{uv}(\bar{R}-\bar{R}')$ is exactly the same as in the original

equilibrium, and so all phonon frequencies would be unchanged. We must include anharmonic effects

to describe thermal expansion.

● Ionic crystals (Example)

● In an ionic crystal, the interactions

between ions are dominated
 by the Coulomb interaction

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$\frac{\pm q^2}{|\vec{R}-\vec{R}'|}$ For small displacements,

one has

$$\frac{1}{|\vec{R}-\vec{R}'+\vec{x}|} \approx \frac{1}{|\vec{R}-\vec{R}'|} \left(1 - \frac{(\vec{R}-\vec{R}') \cdot \vec{x}}{|\vec{R}-\vec{R}'|^2} + \frac{3x_{\parallel}^2 - x_{\perp}^2}{2|\vec{R}-\vec{R}'|^3} + \dots \right)$$

Thus $\bar{C}(\vec{R}-\vec{R}') = \frac{\partial^2 U}{\partial \vec{R} \partial \vec{R}'} \propto \frac{1}{|\vec{R}-\vec{R}'|^3}$

Under a rescaling of the lattice spacing a $C \propto a^{-3}$.

$$\omega_{KS} = \sqrt{\frac{\tilde{C}(K)}{m}} \propto a^{-3/2} \propto V^{-1/2}$$

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$$\gamma = -\frac{\partial \ln \omega}{\partial \ln V} = \frac{1}{2}$$

Experimentally, γ ranges from 0.28 in KI at low temperatures to 1.71 in NaI at room temperature. Thus the short range repulsion of the ion cores also plays an important role.