

Monatomic Crystals

Molecules or atoms in a crystal vibrate about their equilibrium position which are arranged in a regular lattice.

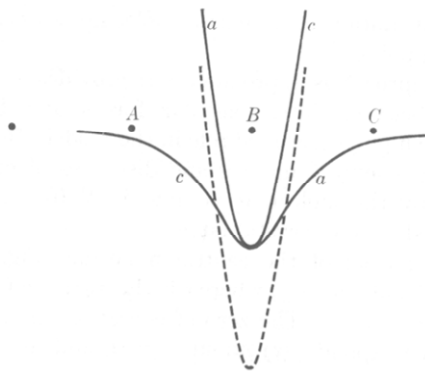
Intermolecular forces, as well as T and p determine the spacing and the nature of the motion.

In the simplest statistical mechanical treatment of a crystal, the system can be decomposed into independent subsystems - the normal modes of vibration.

Einstein Model - qualitatively correct.
Debye Approximation - more accurate.

Einstein Model

1. Each molecule is surrounded by a group of nearest neighbors and a more distant group of next nearest neighbors.
2. A central molecule vibrates in the vicinity of its lattice point in a force field which is the sum of the separate forces of all the surrounding molecules.
3. For inert gas atoms, the forces are dispersion type (van der Waals) and are rather short range.
4. By definition, the potential energy function is minimized when the atom is at its lattice point.
5. The potential energy increases as the molecule departs from its equilibrium position.



Curve "a" is the potential energy function due to the A-B interaction.

Curve "c" is the potential energy function due to the B-C interaction.

The dashed line shows the sum of the interactions on the central atom, B, assuming A and C are fixed.

Vibrational Degrees of Freedom

Each molecule has 3 degrees of freedom - these are translations which have degenerated into vibration.

If the temperature is low enough, the vibrations are small.

At higher temperatures, vibration is more violent.

Lattice imperfections and molecular migrations become more frequent. Eventually the crystal melts.

In the Einstein model, each molecule vibrates in its own cell independently. Other molecules are frozen in their equilibrium positions.

In reality, the motions of neighbors are coupled.

Energy Potential at the Central Atom

In the Einstein model, the potential is taken to be spherically symmetric; hence, the vibrational motion is isotropic about the equilibrium point.

The distances to neighbors is determined by the molecular volume, V/N .

We expand the molecular potential about the equilibrium point:

$$\varphi(r) = \varphi(0) + \frac{1}{2}fr^2 + \dots \quad \text{or} \quad \varphi(r) - \varphi(0) = \frac{1}{2}f(x^2 + y^2 + z^2)$$

Where (x, y, z) are the coordinates w.r.t. the lattice point and the force constant is

$$f = \left(\frac{\partial^2 \varphi(r)}{\partial r^2} \right)_{r=0}$$

Einstein Model

The frequency of the Harmonic motion is just

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$$

Since the force constant f is a function of V/N , so will be the vibrational frequency.

In the Einstein model, the Hamiltonian for the system of N independent oscillators is just the sum of N equivalent Hamiltonians, one for each molecule. All together we have a collection of $3N$ independent 1-D oscillators with classical frequency ν .

The partition function for the canonical ensemble of $3N$ oscillators is:

$$Q(N, V, T) = e^{-N\phi(0; V/N)/2kT} q(V/N, T)^{3N}$$

The factor $e^{-N\phi(0; V/N)/2kT}$ is the partition function for a hypothetical system with all molecules at rest at their lattice points.

The energy $N\phi(0; V/N)/2$ is the potential energy relative to the system at infinite separation of all molecules - i.e. all molecules infinitely separated and at rest.

The factor of 2 comes from the additive effects of neighbors on either side - the potentials are additive. Each neighbor contributes $N\phi(0; V/N)/2$ to the potential energy.

The energy levels are given by $\epsilon_n = (n + 1/2)h\nu$, $n = 0, 1, 2, \dots$

$$\text{Thus, } q = e^{-h\nu/2kT} \sum_{n=0}^{\infty} e^{-nh\nu/kT} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}}$$

The parameter Θ_v is called the characteristic temperature; it is a function of V/N .

Typically, Θ_v is on the order of 300 K and ν is of the order of $5 \times 10^{12} \text{ s}^{-1}$.

This frequency is about ten times smaller than the internal vibrational frequency of an isolated diatomic molecule;

In a diatomic molecule, the forces are covalent - much stronger than the dispersive forces.

At high temperatures, $T \gg \Theta_v$;

$$q = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \rightarrow \frac{1 - \frac{\Theta_v}{2T} + \dots}{1 - \left[1 - \frac{\Theta_v}{T} + \dots\right]} \approx \frac{T}{\Theta_v} = \frac{kT}{h\nu}$$

As $T \rightarrow 0$; $q \rightarrow e^{-\Theta_v/2T}$

Each oscillator has its zero point energy.

Thermodynamic properties:

$$Q(N, V, T) = e^{-N\phi(0; V/N)/2kT} q(V/N, T)^{3N}$$

$$A = -kT \ln Q = \frac{N\phi(0)}{2} - 3NkT \ln \left(\frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \right)$$

$$\begin{aligned} E &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V} = kT^2 \left(\frac{\partial \ln Q}{\partial (\Theta_v/T)} \right)_{N, V} \left(\frac{\partial (\Theta_v/T)}{\partial T} \right) \\ &= \frac{N\phi(0)}{2} + \frac{3Nh\nu}{2} + 3NkT \ln \left(\frac{\Theta_v/T}{e^{\Theta_v/T} - 1} \right) \end{aligned}$$

At high temperatures, $E \rightarrow 3NkT$. This is the negative of the heat of sublimation of an Einstein crystal at 0 K.

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{N, V} = 3Nk \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}$$

The heat capacity is a universal function of Θ_v/T .

The heat capacity curves for different crystals can be superimposed with compression or expansion of the temperature axis. \Rightarrow Example of the law of corresponding states.

For two crystals with Θ_{v1} and Θ_{v2} , if the first crystal is at T_1 , then the corresponding temperature for the 2nd crystal is just

$$T_2 = T_1 \frac{\theta_{v1}}{\theta_{v2}}$$

The two crystals have the same C_v/Nk

Heat Capacity Temperature Dependence

The limiting values of the heat capacity given by the Einstein model is:

$$C_v \rightarrow 3Nk \quad \text{as } T \rightarrow \infty$$

This is in agreement with the Law of Dulong and Petit, but

$$C_v \rightarrow 3Nk \left(\frac{\theta_v}{T} \right)^2 e^{-\theta_v/T} \quad \text{as } T \rightarrow 0$$

Goes to zero too quickly. Experimentally, $C_v \propto T^3$.

The low temperature behavior is correctly described by Debye's theory.

Thermodynamic Functions in the Crystalline Phase

For a condensed phase such as a crystal, pV is much smaller than A , E , etc.

From the thermodynamic relations,

$$G = N\mu = H - TS$$

$$H = E + pV$$

$$G = E + pV - TS$$

$$A = E - TS$$

We deduce that

$$G = N\mu \approx A$$

$$H = E$$

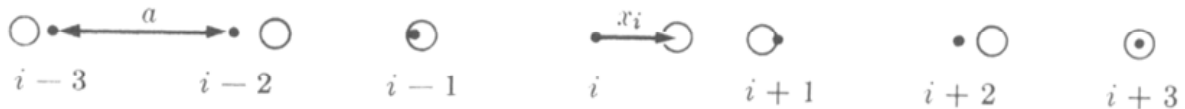
Thus,

$$\mu = \frac{\varphi(0)}{2} - 3kT \ln \left(\frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \right)$$

General Treatment of Vibrations

Exact treatment of vibrations in a monatomic crystal.

Consider a 1-dimensional crystal with lattice spacing a , and with only nearest and next nearest neighbor interactions being significant:



The distance between the i^{th} atom and the $i+1^{\text{th}}$ atom is:

$$\Delta x_{i+1} = a + x_{i+1} - x_i$$

The distance between the i^{th} atom and the $i+2^{\text{th}}$ atom is:

$$\Delta x_{i+2} = 2a + x_{i+2} - x_i$$

Comments on the potential:

$$U(x) = \sum_{i=1}^N \left[u(a + x_{i+1} - x_i) + u(2a + x_{i+2} - x_i) \right]$$

1. With all atoms at their lattice points, $x_i = 0$,

$$U(0) = u(a) + u(2a)$$

This corresponds to $N\phi(0)/2$ in the Einstein model.

2. The force on the j^{th} molecule is given by $F = ma$,

$$\begin{aligned} m \frac{d^2 x_j}{dt^2} &= - \frac{\partial U}{\partial x_j} \\ &= -u'(a + x_j - x_{j-1}) - u'(2a + x_j - x_{j-2}) \\ &\quad + u'(a + x_{j+1} - x_j) + u'(2a + x_{j+2} - x_j) \end{aligned}$$

The motion of the j^{th} atom is coupled to the motion of neighboring atoms. To uncouple the motion, as required by the Einstein model, assume as an approximation that the neighboring atoms are fixed:

$$m \frac{d^2 x_j}{dt^2} = -u'(a + x_j) - u'(2a + x_j) + u'(a - x_j) + u'(2a - x_j) = -\frac{d\phi(x_j)}{dx_j}$$

Here, $\phi(x_j)$ is the potential in the Einstein model:

$$\phi(x_j) = u(a + x_j) + u(2a + x_j) + u(a - x_j) + u(2a - x_j)$$

Returning to $U(x) = \sum_{i=1}^N [u(a + x_{i+1} - x_i) + u(2a + x_{i+2} - x_i)]$

We can expand this potential using a Taylor series. This will be valid for small excursions from equilibrium.

Let $\delta_i = x_{i+1} - x_i$

and $\eta_i = x_{i+2} - x_i$

Expanding $u(a + \delta_i)$ around a :

Linear terms vanish at $x_i=0$ because the potential $U(x)$ has a minimum at $x_i=0$ for all i .

$$u(a + \delta_i) = u(a) + u'(a)\delta_i + \frac{1}{2}u''(a)\delta_i^2 + \dots$$

$$= u(a) + \frac{1}{2}u''(a)(x_{i+1} - x_i)^2 + \dots$$

$$= u(a) + \frac{1}{2}u''(a)[x_{i+1}^2 + x_i^2 - 2x_{i+1}x_i] + \dots$$

$$u(2a + \eta_i) = u(2a) + u'(2a)\eta_i + \frac{1}{2}u''(2a)\eta_i^2 + \dots$$

$$= u(2a) + \frac{1}{2}u''(a)(x_{i+2} - x_i)^2 + \dots$$

$$= u(2a) + \frac{1}{2}u''(a)[x_{i+2}^2 + x_i^2 - 2x_i x_{i+2}] + \dots$$

The potential energy $U(x)$ is therefore

$$U(x) = U(0) + \frac{1}{2}u''(a) \sum_i [x_{i+1}^2 + x_i^2 - 2x_{i+1}x_i] + \dots$$

$$+ \frac{1}{2}u''(2a) \sum_i [x_{i+2}^2 + x_i^2 - 2x_{i+2}x_i] + \dots$$

The total energy is a sum of the kinetic and potential energies.

The kinetic energy is just $T = \sum_i m\dot{x}_i^2 / 2$

The total energy, $H = T(\dot{x}) + U(x)$

Contains cross terms such as $x_i x_{i-1}$ and is not separable. Thus, we do not have a system of independent subsystems.

Normal Coordinates

It is possible to transform the original coordinates by a linear transformation to a new set of coordinates such that the energy in the new coordinates has a diagonalized potential energy.

$$\xi_1 = \alpha_{11}x_1 + \alpha_{12}x_2 + \dots + \alpha_{1N}x_N$$

$$\xi_2 = \alpha_{21}x_1 + \alpha_{22}x_2 + \dots + \alpha_{2N}x_N$$

$$\vdots$$

$$\xi_N = \alpha_{N1}x_1 + \alpha_{N2}x_2 + \dots + \alpha_{NN}x_N$$

In this new coordinate system, the energy can be written

$$H(\xi, \dot{\xi}) = U(0) + \frac{1}{2} \sum_i f_i \xi_i^2 + \frac{1}{2} \sum_i M_i \dot{\xi}_i^2$$

Where the f_i are effective force constants (functions of the coefficients of the quadratic terms) and M_i are effective masses, functions of m .

For each of the normal coordinates there is an energy contribution

$$H_i = \frac{1}{2} f_i \xi_i^2 + \frac{1}{2} M_i \dot{\xi}_i^2 \quad \text{to } H-U(0).$$

Therefore, the Shrodinger equation is separable into N independent Schrodinger equations. The Hamiltonian for the ith normal mode yields nondegenerate energy levels given by

$$\varepsilon_{in} = (n + 1/2)h\nu_i, \quad n = 0, 1, 2, \dots \quad \text{where} \quad \nu_i = \frac{1}{2\pi} \sqrt{\frac{f_i}{M_i}}$$

The normal modes form a system of N independent subsystems. Hence we can form the grand canonical partition function.

$$Q = e^{-U(0)/kT} \prod_{i=1}^N q(\theta_i)$$

Where $\theta_i = h\nu_i/k$ is the characteristic temperature of the i^{th} normal mode.

The factor $e^{-U(0)/kT}$ included in Q is the zero of energy corresponding to infinitely separated atoms at rest.

Now the problem has been reduced to one of finding the N frequencies ν_i .

Partition function

In 3D, we have 3N-6 normal modes $\sim 3N$ for large N.

$$Q = e^{-U(0)/kT} \prod_{i=1}^{3N} q(\theta_i) = e^{-N\phi(0)/2kT} \prod_{i=1}^{3N} q(\theta_i)$$

Note that $\phi(0)$ and θ_i are functions of V/N .

Because of the large number of frequencies, we can consider there to be a continuous frequency distribution,

$g(\nu)d\nu$ is the number of normal modes with frequencies between ν and $\nu+d\nu$.

$$\text{Using } q = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}$$

$$-\ln Q = \frac{N\phi(0)}{2kT} + \int_0^{\infty} \left[\ln(1 - e^{-h\nu/kT}) + \frac{h\nu}{2kT} \right] g(\nu) d\nu$$

where $\int_0^{\infty} g(\nu) d\nu = 3N$.

Heat Capacity

$$C_v = k \int_0^{\infty} \frac{(h\nu/kT)^2 e^{h\nu/kT} g(\nu)}{(e^{h\nu/kT} - 1)^2} d\nu$$

The problem is that we cannot explicitly calculate any thermodynamic quantities without having the particular form of $g(\nu)$.

It also becomes clear that this expression reduces to C_v in Einstein's model if $g(\nu)$ is taken to be a Dirac delta function, $\delta(\nu - \nu^*)$, normalized according to

$$\int_0^{\infty} \delta(\nu - \nu^*) d\nu = 3N$$