We have one dimensional chain of identical atoms with mass m. Nearest atoms are connected by the spring with elastic constant k and equilibrium distance between nearest neighbor is equal a. We need to describe the motion of atoms and calculate specific heat of the chain. We assume that total number of atoms in chain is N. Then the equation of motion for atom n is follows:

$$m \cdot \ddot{u}_n = F_n \quad ,$$

here F_n is a force acting on atom n and u_n – displacement of this atom from equilibrium position. The total potential energy of all deformed springs can be calculated so (classic equation for Hooke's force):

$$U = \frac{k}{2} \sum_{k=1}^{N} (u_k - u_{k-1})^2$$

The F_n can be calculated directly from formulas:

$$F_n = -\frac{dU}{du_n} = k \cdot (u_{n+1} - 2u_n + u_{n-1})$$

The equation of motion is look like so:

$$\ddot{u}_n = \frac{k}{m} \cdot (u_{n+1} - 2u_n + u_{n-1})$$

REMARK.

The total energy of the interacting atom can be decomposed into a power series (Taylor series) by small atomic displacements u_n.

$$U = U(u_n = 0) + \sum_n \left(\frac{dU}{du_n}\right)_{un=0} \cdot u_n + \frac{1}{2} \sum_{n,n'} \left(\frac{d^2U}{du_n du_{n'}}\right)_{u_n, u_n'=0} u_n u_{n'} + \ldots$$

The second member is equal to zero because atoms are located in their equilibrium position

$F_n = -\left(\frac{dU}{du_n}\right)_{u_n=0} = 0$. In this case $U = U(u_n = 0) + \frac{1}{2} \sum_{n,n'} \left(\frac{d^2U}{du_n du_{n'}}\right)_{u_n, u_n'=0} u_n u_{n'} + \ldots$.

After substitution $\left(\frac{dU}{du_n}\right)_{un=0} = \Phi_{n,n'}$ we get $U = U(u_n = 0) + \frac{1}{2} \sum_{n,n'} \Phi_{n,n'} u_n u_{n'} + \ldots$.

For harmonic approximation (we take into the account only quadratic members). The force acting on atom n now could be directly calculated so:

$F_n = -\frac{dU}{du_n} = -\frac{1}{2} \sum_{n'} \Phi_{n,n'} u_{n'}$. If we assume the interaction only nearest atoms this equation can be simplified by this way:

1. $\Phi_{n,n'} = k$, $for\, n \neq n'$, for non diagonal elements k- elastic constant of the spring.
2. The diagonal elements of this matrix can be calculated so, if all atoms were displaced on the same distance u_0 (whole crystal translation on the distance u_0) , F_n must be equal to 0. It means that

$F_n = -\frac{dU}{du_n} = -\frac{1}{2}\sum_{n'} \Phi_{n,n'} u_0 = -\frac{u_0}{2}\sum_{n'} \Phi_{n,n'} = 0$ or $\sum_{n'} \Phi_{n,n'} = 0$ and *finally* $\Phi_{n,n} = -\sum_{n' \neq n} \Phi_{n,n'}$.
For our simple model $\Phi_{n,n} = -2k$. And for force acting on atom number n we obtain the same equation.

$$F_n = -\frac{1}{2}\left(k \cdot u_{n+k} + k \cdot u_{n+1} + k \cdot u_{n-1} + k \cdot u_{n-1} + 2 \cdot u_n \Phi_{n,n}\right)$$

END OF REMARK

The solution of this first order differential equation can be represented as:

$$u_n(x,t) = A \cdot e^{i(\omega t + k \cdot x)} = A(t) \cdot e^{ik \cdot x} \quad \text{,and} \quad A(t) = A \cdot e^{i\omega \cdot t}$$

or if we take into account that the chain is discrete and coordinates of atoms can be calculated by this way $x_n = n \cdot a$

$$u_n(t) = A \cdot e^{i(\omega \cdot t + k \cdot n \cdot a)} = A(t) \cdot e^{ik \cdot n \cdot a}$$

after substitution and calculation of the derivatives we get equation for frequency:

$$\omega^2 = \frac{2k}{m}(1 - \cos(k \cdot a)) \quad \text{, or} \quad \omega^2 = \frac{4k}{m}\sin^2\left(\frac{k \cdot a}{2}\right) \quad \text{and finally} \quad \omega = \omega_0 \left|\sin\left(\frac{k \cdot a}{2}\right)\right|$$

here $\omega_0^2 = \frac{4k}{m}$.

To calculate the valid values for k-wave vector we apply the periodic boundary condition. It means that if total number of atom in the chain is equal to N, so the atom with number n and n+N are equal. Or by other words $u_n = u_{n+N}$. The total length of chain is L=N a.
After substitution we have:

$$A \cdot e^{i(\omega \cdot t + k \cdot n \cdot a)} = A \cdot e^{i(\omega \cdot t + k \cdot (n+N) \cdot a)} \quad \text{or} \quad e^{ik \cdot N \cdot a} = 1 \quad \text{bu it is possible only if} \quad k = \frac{2\pi}{L} n, \ \textit{here} \ n \in Z \ .$$

Now we know how the wave vectors can be calculated and we be able to simplify the calculation of frequencies. Do no forget that k-vector is discrete parameter with the step of changes $\Delta k = \frac{2\pi}{L}$.

This function

$$\omega = \omega_0 \left|\sin\left(\frac{k \cdot a}{2}\right)\right|$$

is a periodic with period of π. It means that make sense to take into account only only non equvalent values of wave vector. The nonequivalent values of k-vector are located in regions

$$[0...2\cdot\pi] \text{ or } [-\frac{\pi}{2}...+\frac{\pi}{2}] \quad .$$

The total number of possible values for k-vector in this region is equal to N. Each k-vector value corresponds to individual longitudinal harmonic waves propagating in chain. Each wave in the crystal should be counted only once. The harmonic waves are form the full set of basic vectors in the space of atomic vibrations. The harmonic waves are form the full set of basis vectors in the space of atomic vibrations. It is means that vibration of each individual atom can be represented as a linear combination of these harmonic waves. By the other words

$$u_n(t)=\sum_{k=-\pi/2}^{+\pi/2} A_k\cdot e^{i(\omega(k)t+k\,a\,n)} \quad .$$

To simplify further calculations of specific heat I want to define an additional function, density of vibrations or density of states $g(\omega)=\frac{d\,n}{d\,\omega}$. The physical meaning is this function dn=g(ω) dω is it give the value of harmonic waves dn in region of frequencies from ω to ω+dω. For example the nex integral give us $\Delta n=\int_{\omega_1}^{\omega_2} g(\omega)\,d\,\omega$ number of harmonic waves, vibrations in region of frequencies from ω_1 to ω_2, and $N=\int_0^{\omega_0} g(\omega)\,d\,\omega$.

By using expression $k=\frac{2\pi}{L}n$ or $dk=\frac{2\pi}{L}dn$ after substitution dn we obtain $g(\omega)=\frac{L}{2\pi}\cdot\frac{1}{\left|\frac{d\,\omega}{dk}\right|}$. Derivative can be calculated directly $\frac{d\,\omega}{dk}=\omega_0\frac{a}{2}\cos(\frac{ka}{2})$. After substitution into previous equation we finally obtain: $g(\omega)=\frac{N}{\pi}\cdot\frac{1}{\sqrt{\omega_0^2-\omega^2}}$.

As you see this function can be used to substitute integration over the wave vector by integration over the frequency. Corresponding relation is: $dk=\frac{2\pi}{L}g(\omega)\,d\,\omega$.

Now we need to calculate the total energy of chain. This equation looks like so:

$$E=E_{kin}+E_{pot}=\sum_n \frac{m\cdot u_n^2}{2}+\frac{k}{2}\sum_n (u_n-u_{n-1})^2 \quad .$$

Lets start from calculation of kinetic energy by substitution $u_n(t)=\sum_{k=-\pi/2}^{+\pi/2} A_k\cdot e^{i(\omega(k)t+k\,a\,n)}$

The final result is $E_{kin}=\frac{m}{2}\sum_k \dot{A}_k^{\,2}$.

The potential energy can be calculated by the same way and after some simplifications:

$$E_{pot}=\frac{1}{2}\sum_k \omega(k)^2 A_k^2$$

and the total energy in harmonic-waves presentation is:

$$\frac{1}{2}\sum_k \{m\dot{A}_k^{\,2}+m\,\omega(k)^2 A_k^2\} \quad .$$

As you see the vibrating chain of atoms in this representation is looks like a set of harmonic oscillators, for each value of k correspond individual harmonic wave or harmonic oscillator. Total number of different oscillator is equal to N. It means that the total energy of chain can be calculated by formulas from quantum mechanics $E_k = \hbar\omega\left(n+\frac{1}{2}\right)$

$E = \sum_k \hbar\omega(k)\left(n_k+\frac{1}{2}\right) = \sum_k \hbar\omega(k)\left(<n_k>+\frac{1}{2}\right)$. Here $<n_k>$ is a average value of quantum number n which can be calculated from Bose-Einstein distribution.

$$E = \frac{L}{2\pi}\int_{-\pi/2}^{+\pi/2} \frac{\hbar\omega(k)}{e^{\frac{\hbar\omega(k)}{kT}}-1}dk = \frac{2N}{\pi}\int_0^{\omega_0} \frac{\hbar\omega}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)\sqrt{\omega_0^2-\omega^2}}d\omega \quad .$$