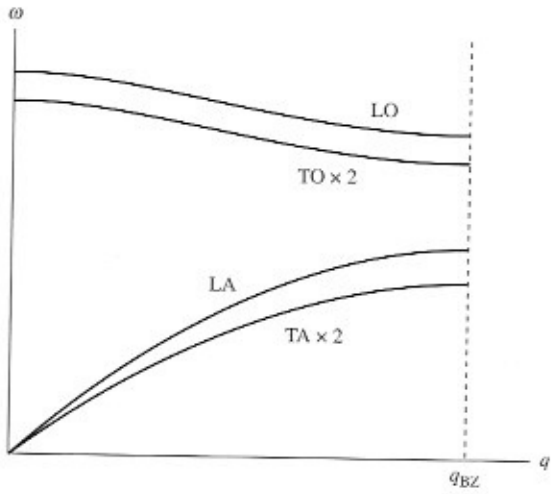

Figure 4.8 Lattice vibration dispersion curve for KBr. The transverse branches are doubly degenerate.

4.2 Second quantization and phonons

We now turn to an elementary excitation view of lattice vibrational properties by associating phonons with the vibrational modes. Phonons are viewed as being particle-like and wave-like in analogy with electromagnetic radiation. We begin by considering a simple one-dimensional harmonic oscillator, satisfying the equation

$$m\ddot{x} = -\gamma x. \tag{4.41}$$

The solution is $x(t) = x_0 e^{-i\omega t}$, where $\omega = \sqrt{\gamma/m}$ for spring constant γ and mass m. If we take a quantum view starting with the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}\gamma x^2, \tag{4.42}$$

then the energy levels are

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad (n = 0, 1, 2, \ldots). \tag{4.43}$$

It is convenient to take a second quantized view of this problem using creation and annihilation operators. The standard approach is to form a linear combination of the coordinate and momentum variables, x and p, and form new variables, a and $a^\dagger$, such that these variables satisfy the commutation relation

$$[a, a^\dagger] = 1. \tag{4.44}$$

The combinations of x and p for a and $a^\dagger$ are

$$a = \frac{1}{\sqrt{2\hbar\omega m}}(p - im\omega x) \tag{4.45}$$

and

$$a^\dagger = \frac{1}{\sqrt{2\hbar\omega m}}(p + im\omega x). \tag{4.46}$$

This choice satisfies Eq. (4.44) since $[x,p] = i\hbar$. Replacing x and p in Eq. (4.42) by expressing them in terms of a and $a^\dagger$, using Eqs. (4.45) and (4.46), yields

$$H = \frac{1}{2}\hbar\omega(aa^\dagger + a^\dagger a). \tag{4.47}$$

A matrix representation for a and $a^\dagger$ can be introduced based on labeling states by the index n. We have the following eigenvalue equations for the harmonic oscillator

$$a\,|n\rangle = \sqrt{n}\,|n-1\rangle \tag{4.48}$$

and

$$a^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle, \tag{4.49}$$

which are consistent with Eq. (4.44). In addition, Eqs. (4.48) and (4.49) give

$$a^\dagger a\,|n\rangle = n\,|n\rangle, \tag{4.50}$$

and then, using Eq. (4.47), we have

$$H\,|n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega\,|n\rangle = E_n\,|n\rangle. \tag{4.51}$$

From these essential features of the simple one-dimensional harmonic oscillator, we can propose a picture of excitations involving the creation and destruction of quanta in various states and the view of representing a state using the occupation number corresponding to specific quanta. This concept involves the setting up of a many-body state by operating on a vacuum state with creation and destruction operators to increase or decrease the number of particles in a given state. The state vector $\Psi_{n_1,n_2,\ldots,n_i\ldots}$ represents a state with n_1 particles in state 1, n_2 particles in state 2, and so on. The creation operators $a_i^\dagger$ repeatedly acting on the vacuum state $|0\rangle$ can produce this state vector. Also, when the destruction operator a_i operates on the state vector, it destroys a particle in the ith state. There is an overall factor such that

$$a_i\Psi_{n_1,n_2,\ldots,n_i\ldots} = \sqrt{n_i}\Psi_{n_1,n_2,\ldots,n_i-1\ldots}, \tag{4.52}$$

$$a_i^\dagger\Psi_{n_1,n_2,\ldots,n_i\ldots} = \sqrt{n_i+1}\Psi_{n_1,n_2,\ldots,n_i+1\ldots}, \tag{4.53}$$

$$a_i^\dagger a_i\Psi_{n_1,n_2,\ldots,n_i\ldots} = n_i\Psi_{n_1,n_2,\ldots,n_i\ldots}. \tag{4.54}$$

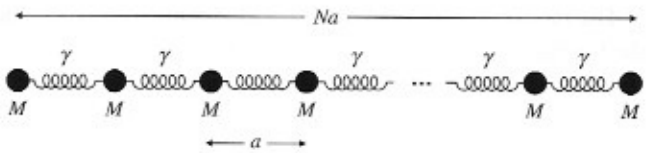

Figure 4.9 Finite linear chain with nearest-neighbor interactions.

Therefore, the operator $\hat{n}_i = a_i^\dagger a_i$ measures the number of particles in the ith state, and it is called the number operator.

Using this short description of second quantization and the occupation number representation for the state of a system, we can go beyond the simple harmonic oscillator and treat the model of interacting atoms, which we considered before, to represent lattice vibrations in a one-dimensional solid. This model uses a linear chain of N atoms of length $L = Na$ with nearest-neighbor interactions (Fig. 4.9). Unlike the harmonic oscillator case, the "extension of the springs" depends on the relative displacements of the atoms. Hence, a simple real-space Hamiltonian composed of a combination of the squares of position and momentum is not possible. However, a decoupling occurs if we use a Fourier transformation of the original Hamiltonian, and this will lead us to the form we need.

We begin with the Hamiltonian containing the kinetic and potential energies expressed in terms of real-space momenta p_n and coordinates ξ_n,

$$H = \frac{1}{2M}\sum_n p_n^2 + \frac{1}{2}\gamma \sum_n (\xi_{n+1} - \xi_n)^2, \tag{4.55}$$

where

$$\left[\xi_n, p_{n'}\right] = i\hbar\delta_{n,n'}. \tag{4.56}$$

As stated above, the desired form for the Hamiltonian is $H = \sum_k H_k$.

To accomplish this, we Fourier-transform the coordinate

$$\xi_n = \frac{1}{\sqrt{N}}\sum_k \xi_k e^{ikna}, \tag{4.57}$$

and

$$\xi_k = \frac{1}{\sqrt{N}}\sum_n \xi_n e^{-ikna}. \tag{4.58}$$

Using PBCs,

$$k = \frac{2\pi\ell}{Na} = \frac{2\pi\ell}{L}, \tag{4.59}$$

with $-\frac{N}{2} < \ell \leq \frac{N}{2}$. Since ξ_n is Hermitian,

$$\xi_k = \xi_{-k}^\dagger. \tag{4.60}$$

The momentum p_k that is canonically conjugate to ξ_k is not obvious. To find it, we use the Lagrangian formalism. For the Lagrangian

$$\mathcal{L}([\xi_k, \dot{\xi}_k]),$$

the canonically conjugate momentum becomes

$$p_k = \frac{\partial \mathcal{L}}{\partial \dot{\xi}_k}.$$

Using

$$\sum_n e^{i(k+k')na} = N\delta_{k+k',0}, \tag{4.61}$$

then the kinetic energy is T, with

$$\begin{aligned} T &= \frac{M}{2}\sum_n (\dot{\xi}_n)^2 \\ &= \frac{M}{2}\frac{1}{N}\sum_{k,k',n} \dot{\xi}_k \dot{\xi}_{k'} e^{i(k+k')na} \\ &= \frac{M}{2}\sum_k \dot{\xi}_k \dot{\xi}_{-k}. \end{aligned} \tag{4.62}$$

Similarly, the potential energy (PE) becomes

$$\mathrm{PE} = \frac{1}{2}\gamma \sum_n (\xi_{n+1} - \xi_n)^2 = \gamma \sum_k \xi_k \xi_{-k}(1 - \cos ka), \tag{4.63}$$

and the Lagrangian has the form

$$\mathcal{L} = \frac{M}{2}\sum_k \dot{\xi}_k \dot{\xi}_{-k} - \gamma \sum_k \xi_k \xi_{-k}(1 - \cos ka). \tag{4.64}$$

Hence, the conjugate momentum is

$$p_k = \frac{\partial \mathcal{L}}{\partial \dot{\xi}_k} = M\dot{\xi}_{-k}. \tag{4.65}$$

Using Eq. (4.58),

$$\xi_{-k} = \frac{1}{\sqrt{N}}\sum_n \xi_n e^{-i(-k)na},$$

and we have

$$p_k = \frac{1}{\sqrt{N}}\sum_n p_n e^{ikna}, \tag{4.66}$$

thus

$$p_k^\dagger = p_{-k}. \tag{4.67}$$

Finally, the Hamiltonian (using the results for the vibration frequency obtained in the last section) is

$$H = \frac{1}{2}\sum_k \left[\frac{p_k p_{-k}}{M} + \underbrace{2\gamma\,(1-\cos ka)}_{M\omega_k^2}\xi_k\xi_{-k} \right] \tag{4.68}$$

$$= \sum_k \left[\frac{1}{2M} p_k^\dagger p_k + \frac{M\omega_k^2}{2}\xi_k^\dagger \xi_k \right], \tag{4.69}$$

and

$$H = \sum_k H_k,$$

which was our objective.

Using the relations above, we can show that

$$[\xi_k, p_{k'}] = i\hbar\delta_{k,k'}. \tag{4.70}$$

If we now define

$$a_k^\dagger = \frac{1}{\sqrt{2\hbar M\omega_k}}(M\omega_k\xi_k^\dagger - ip_k) \tag{4.71}$$

and

$$a_k = \frac{1}{\sqrt{2\hbar M\omega_k}}(M\omega_k\xi_k + ip_k^\dagger), \tag{4.72}$$

then

$$[a_k, a_{k'}^\dagger] = \delta_{k,k'} \tag{4.73}$$

and

$$[a_k, a_{k'}] = [a_k^\dagger, a_{k'}^\dagger] = 0. \tag{4.74}$$

Following our earlier description for the simple harmonic oscillator, we now have

$$H = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right)$$

and

$$\omega_k = \sqrt{\frac{2\gamma}{M}}(1-\cos ka). \tag{4.75}$$

We can now make the comparison with the previous description for the simple harmonic oscillator. The operators $a_k^\dagger$ and a_k create and destroy quanta (phonons) in the state k. The number operator $\hat{n}_k = a_k^\dagger a_k$ measures the number of phonons n_k in the state k. The energy

$$E_k = \left(n_k + \frac{1}{2}\right)\hbar\omega_k$$

is viewed as the excitation energy of n_k phonons of energy $\hbar\omega_k$ plus the ground-state energy (zero-point motion $\frac{1}{2}\hbar\omega_k$). The total energy of the vibrating system of cores is the ground-state energy plus the energy of a group of independent phonons excited above the ground state.

For a given k, there is a quantized vibrational or sound wave mode of wavevector k and energy $\hbar\omega_k$. A sound wave with wavevector k is described by n_k phonons excited above the ground state. Therefore, a statement in common use that a phonon is a quantized sound wave is incorrect. It takes n_k phonons to describe a sound wave. The many-body state $|n_{k_1}, n_{k_2}, \ldots\rangle$ for phonons in different k-states can be constructed using creation operators acting on the vacuum $|0\rangle$,

$$|n_{k_1}, n_{k_2}, \ldots\rangle = (a_{k_1}^\dagger)^{n_{k_1}} (a_{k_2}^\dagger)^{n_{k_2}} \ldots |0\rangle\,. \tag{4.76}$$

The generalization of the one-dimensional case with vibrating cores (in the harmonic approximation) with r atoms per cell in d dimensions leads to the Hamiltonian

$$H = \sum_{\lambda\mathbf{k}} \hbar\omega_{\lambda\mathbf{k}} \left(a_{\lambda\mathbf{k}}^\dagger a_{\lambda\mathbf{k}} + \frac{1}{2}\right), \tag{4.77}$$

where λ is the phonon branch index ($\lambda = 1, 2, \ldots, d \times r$) and $\omega_{\lambda\mathbf{k}}$ are the frequencies from diagonalizing the dynamical matrix.

To generalize, what we have done is to consider the Hamiltonian

$$H = \sum_i H_i(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i,j} V(\mathbf{r}_i, \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j), \tag{4.78}$$

which we then transform into the following:

$$H = E_0 + \sum_{\mathbf{k}} E_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \Delta E. \tag{4.79}$$

The first term, E_0, in Eq. (4.79) is the ground-state energy, the second term represents the energy of the elementary excitations, and the third term, ΔE, is the residual energy representing the interactions between the elementary excitations with terms involving more creation and destruction operators. This term can be expressed in terms of lifetimes for individual states $\mathbf{k}$, $\tau_{\mathbf{k}} \sim \hbar/\Delta E_{\mathbf{k}}$. Hence $\tau_{\mathbf{k}}$ measures the decay time of an excitation. For this picture of viewing a system in terms of elementary excitations (quasiparticles and collective excitations) to be useful, we require that

$$\Delta E_{\mathbf{k}} < E_{\mathbf{k}}. \tag{4.80}$$

When Eq. (4.80) is satisfied, then we can view our system as a collection of nearly independent excitations, and the properties of a solid can be viewed by considering the properties of a gas of these elementary excitations responding to a probe. In the example of phonons discussed above, $\Delta E = 0$ because we have made the harmonic approximation. Any anharmonic terms in Eq. (4.7) would lead to interactions between phonons.

4.3 Response functions: heat capacity

In many respects, the response functions corresponding to different probes have similar features. The probe could be temperature or EM radiation, for example. The probes excite elementary excitations which then give rise to the response based on the properties of the system. The heat capacity at constant volume $C_V(T)$ is a response function, giving the responses to a temperature probe by describing the T dependence of the energy U of the system when elementary excitations are created.

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V. \tag{4.81}$$

For a gas of phonons, we compute the thermodynamic average energy U using Bose statistics for phonons (since they satisfy the boson commutator relations given in Eqs. (4.73) and (4.74)) with branch index λ, wavevector $\mathbf{q}$, and energy $\hbar\omega_{\lambda,\mathbf{q}}$:

$$U(T) = \sum_{\lambda,\mathbf{q}} \hbar\omega_{\lambda,\mathbf{q}} \left[\langle n_{\lambda,\mathbf{q}}(T)\rangle + \frac{1}{2}\right], \tag{4.82}$$

where the phonon occupation is given by

$$\langle n_{\lambda,\mathbf{q}}(T)\rangle = \frac{1}{e^{\frac{\hbar\omega_{\lambda,\mathbf{q}}}{k_B T}} - 1}. \tag{4.83}$$

Then

$$C_V(T) = \frac{\partial U}{\partial T} = \sum_{\lambda,\mathbf{q}} \hbar\omega_{\lambda,\mathbf{q}} \frac{e^{\frac{\hbar\omega_{\lambda,\mathbf{q}}}{k_B T}} \left(\frac{\hbar\omega_{\lambda,\mathbf{q}}}{k_B T^2}\right)}{\left(e^{\frac{\hbar\omega_{\lambda,\mathbf{q}}}{k_B T}} - 1\right)^2}, \tag{4.84}$$

where k_B is the Boltzmann's constant. For a sample of volume V,

$$\sum_{\mathbf{q}} \to \frac{V}{(2\pi)^3} \int_{BZ} d^3\mathbf{q} \tag{4.85}$$