discussion of the physical quantities which will be considered in the next section.

1.7. CALCULATION OF THE GROUND STATE ENERGY AND THE NEUTRON CROSS-SECTION IN TERMS OF THE PHONON GREEN'S FUNCTION

We can now use the exact Green's function (1.6.10) to calculate the correlation functions (1.4.10) and (1.4.11) which determine the change in ground state energy and the neutron scattering. Using the **k**-space transformation (1.6.4) for $G_{ij}(t)$ we have

$$\Delta E_G = \lim_{t\to 0+} \tfrac{1}{2} iM \sum_{i\neq j} D_{ij} \int_0^1 d\lambda \frac{1}{N} \sum_{\mathbf{k}} G_{\mathbf{k}}(t)\, e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)},$$

and

$$\frac{1}{N} \sum_{i\neq j} D_{ij}\, e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)} = \frac{1}{N} \sum_{j} D_{\mathbf{k}} = D_{\mathbf{k}};$$

hence

$$\Delta E_G = \lim_{t\to 0+} \tfrac{1}{2} iM \int_0^1 d\lambda \sum_{\mathbf{k}} D_{\mathbf{k}} G_{\mathbf{k}}(t). \tag{1.7.1}$$

But, from Eq. (1.6.11),

$$\lim_{t\to 0+} G_{\mathbf{k}}(t) = -\frac{i}{2M\Omega_{\mathbf{k}}};$$

hence

$$\begin{aligned}\Delta E_G &= \tfrac{1}{4} \int_0^1 d\lambda \sum_{\mathbf{k}} D_{\mathbf{k}}/\Omega_{\mathbf{k}} \\ &= \tfrac{1}{4} \sum_{\mathbf{k}} D_{\mathbf{k}} \int_0^1 \frac{d\lambda}{\sqrt{(\Omega_0^2 + \lambda D_{\mathbf{k}})}} \\ &= \tfrac{1}{2} \sum_{\mathbf{k}} \{\sqrt{(\Omega_0^2 + D_{\mathbf{k}})} - \Omega_0\},\end{aligned} \tag{1.7.2}$$

in precise agreement with the result (1.1.12) obtained from the normal mode analysis.

The time correlation function (1.4.11), whose Fourier transform gives the differential neutron scattering cross-section according to Eq. (1.3.10), is [using Eqs. (1.6.13) and (1.6.11) for $t > 0$]

$$\begin{aligned} F(\mathbf{q}, t) &= \frac{iq^2}{N} \sum_{jl} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_j)} \sum_{\mathbf{k}} G_{\mathbf{k}}(t)\, e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_l)} \\ &= \frac{q^2}{2NM} \sum_{jl} \sum_{\mathbf{k}} \frac{1}{\Omega_{\mathbf{k}}}\, e^{-i\Omega_{\mathbf{k}} t}\, e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{R}_l - \mathbf{R}_j)} . \end{aligned} \tag{1.7.3}$$

This expression describes an inelastic scattering process in which one phonon of frequency $\Omega_{\mathbf{k}}$ and wave vector $\mathbf{k}$ is emitted by the incident neutron. The time Fourier transform of Eq. (1.7.3) contains a delta function $\delta(\omega - \Omega_{\mathbf{k}})$, showing that the neutron loses energy $\hbar\Omega_{\mathbf{k}}$, and the target gains energy $\hbar\Omega_{\mathbf{k}}$, in the process. Also the lattice sum in Eq. (1.7.3) is zero unless $\mathbf{q} - \mathbf{k} = \mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector; this relation determines the change in the neutron's momentum and can be interpreted as representing conservation of crystal momentum in the scattering process.

Since the target is at zero temperature, there are no phonons present in equilibrium, and therefore Eq. (1.7.3) contains no terms which correspond to phonon *absorption* by the incident neutron. Such processes appear at non-zero temperature, as will be seen in Chap. 2.

The scattering of slow neutrons from crystals permits a direct experimental determination of the phonon dispersion law. The peaks in the differential cross-section as a function of energy transfer correspond to the frequencies of the phonon modes and, by measuring the cross-section for different values of the momentum transfer $\mathbf{q}$, one can determine the relation between $\Omega_{\mathbf{k}}$ and $\mathbf{k}$ for the phonons. The lattice vibration spectra of many substances have been determined in this way [see Brockhouse (1964)].

For the present problem, in which only harmonic terms were included in the expansion of the lattice potential energy, the iteration series could be summed in closed form because the repeated time integrals in Eq. (1.5.14) are convolutions, corresponding to simple chain diagrams of the form shown in Fig. 1.3. In practice the anharmonic terms, which arise from the higher terms in the expansion of V in powers of the lattice

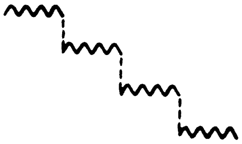

Fig. 1.3. Chain diagram for the harmonic lattice.

displacements, are not negligible (there are indeed features such as the thermal expansion which do not exist at all within the harmonic approximation), and it is therefore an important task of solid-state theory to describe the lattice dynamics of an anharmonic crystal. When anharmonicity is included the perturbation hamiltonian contains products of 3 or more *u* operators. We then have to consider more complicated diagrams such as Fig. 1.4 which cannot be summed

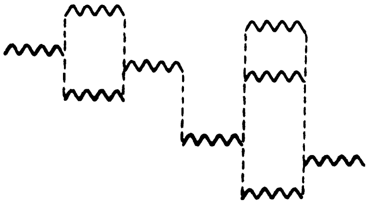

Fig. 1.4. A diagram for the anharmonic lattice.

exactly. It is, however, possible to perform *partial* summations by picking out subsets of diagrams similar in form to those obtained in the harmonic approximation. If one can justify the neglect of the remaining diagrams, one can in this way obtain approximate solutions of the many-body problem. The main physical effect of anharmonicity is to give rise to interactions between the normal modes, which can be described as collision processes in which the number of phonons is not conserved. Thus Fig. 1.4 will contain processes in which two phonons are excited which interact to give one phonon. The effect of such processes is to shift the position of the poles of the single-particle

Green's function: the change in the real part leads to a frequency shift of the phonon modes, and the poles also acquire a finite imaginary part which gives a finite lifetime to the modes. This shows up experimentally as a broadening of the neutron scattering cross-section for one-phonon processes; the delta-function peaks acquire a finite width proportional to the inverse lifetime of the mode. The theory of the subject has been reviewed by Cowley (1963) and the experimental aspects by Martin (1965).

The Green's function approach also provides a powerful method for studying the lattice vibrations of crystals containing defects or impurities of various kinds. The main complication, as compared with the ideal lattice problem, is that the translational invariance property is lost, so that (in 3 dimensions) it is necessary to solve $3N$ equations of motion instead of only 3. Nevertheless, exact solutions can still be obtained in particular cases, and much work has been done on the modes of vibration of a defect lattice [for a review see Maradudin (1964)].