

Chapter 2

Lattice Dynamics at Finite Temperatures

The formalism developed in Chap. 1 enables us to deal with ground state properties of many-body systems. It thus applies to systems which are, in the thermodynamic sense, at zero temperature. In this limit we obtain a theory which is free from the complicating effects of temperature motions and which can be applied to real systems provided that temperature effects are negligible. But there are many interesting properties which cannot be discussed in this way; for example, thermodynamic quantities such as specific heats are zero at $T = 0$, and in the case of other quantities (e.g., magnetic susceptibilities, scattering cross-sections) which are non-zero at $T = 0$ we may wish to study the variation with temperature and with other parameters at finite T . In this chapter we extend the techniques developed in Chap. 1 to deal with non-zero temperatures.

When $T \neq 0$ the ground state expectation values of Chap. 1 are replaced by thermal averages over an appropriate thermodynamic ensemble. [For a summary of relevant thermodynamic formulae, see, for example, Fetter and Walecka (1971), Chap. 2.] The Green's functions which enable us to calculate such averages have more complicated properties than the zero temperature functions (although we shall see that close analogies exist). In particular, we now have to consider two types of Green's function. We first study the so-called *temperature* Green's function, in which the time variable is replaced by a temperature variable. This has a perturbation theory analogous to that developed in Chap. 1, and it allows us to determine the equilibrium thermodynamic properties of the system. We shall use it to determine the free energy of the harmonic lattice at temperature T . For discussing excitations and the response of the system to an external perturbation we need a *time-dependent* Green's function at temperature T ; we shall use such a function to obtain the neutron scattering cross-section at finite temperature. The relation between the two types of Green's function is discussed in Appendix 2.

We adopt a similar approach to that of Chap. 1 and begin by calculat-

ing the lattice free energy by a direct method, using the exact phonon eigenvalues and eigenstates. We then rederive the same result by calculating the temperature Green's function for the problem, and we finally show that the temperature Green's function needed for the free energy also allows us to determine the time-dependent Green's function needed for the neutron scattering cross-section.

2.1. THE FREE ENERGY IN THE HARMONIC APPROXIMATION

If we exclude fluctuation properties, the different ensembles of thermodynamics lead to equivalent results and we can use whichever is most convenient. We shall usually work with the grand canonical ensemble, in which neither the energy nor the number of particles in the system has to be precisely specified. This is the appropriate ensemble for use in a many-body theory expressed in the language of second quantization (see Appendix 1) which allows for the creation and destruction of particles. Furthermore, in some systems (e.g., the quantum condensates in superfluid helium and superconductors) the existence of a variable particle number is more than a mathematical convenience and corresponds to the physical reality of the situation.

In the grand canonical ensemble all the thermodynamic properties can be deduced from the *thermodynamic potential*

$$\Omega(T, V, \mu) = -k_B T \log Z_G, \quad (2.1.1)$$

which is a function of temperature T , volume V , and chemical potential μ . Z_G is the *grand partition function*, defined in terms of the many-body hamiltonian H as a trace

$$Z_G = \text{Tr} e^{-\beta(H - \mu \hat{N})}, \quad (2.1.2)$$

where $\beta = 1/k_B T$ ($k_B =$ Boltzmann's constant) and \hat{N} is the (total) number operator (see Appendix 1). The entropy S , pressure P , and number of particles N in the system are obtained from Ω by differentiation:

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu}, \quad P = - \left(\frac{\partial \Omega}{\partial V} \right)_{T, \mu}, \quad N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V}, \quad (2.1.3)$$

and from these quantities the specific heats, the equation of state, and other thermodynamic relations can be deduced.

In the canonical ensemble (where N is fixed) one deals instead of Ω

with the (Helmholtz) free energy

$$\mathcal{F}(T, V, N) = \Omega + \mu N, \quad (2.1.4)$$

in terms of which the chemical potential is given by

$$\mu = \left(\frac{\partial \mathcal{F}}{\partial N} \right)_{T, V}. \quad (2.1.5)$$

For the phonon system $\mu = 0$ [this is because there is no restriction on the number of phonons, so that the equilibrium state for fixed T and V is obtained by minimizing \mathcal{F} with respect to N , leading to the condition $(\partial \mathcal{F} / \partial N)_{T, V} = 0$]; hence in this case the canonical and grand canonical ensembles are identical. We shall therefore work in this chapter with the free energy

$$\mathcal{F} = -k_B T \log \text{Tr} e^{-\beta H}. \quad (2.1.6)$$

In the limit $T \rightarrow 0$ the trace (which is in general a sum over the eigenvalues of H) reduces to a single term $\exp(-\beta E_G)$, and \mathcal{F} reduces to the ground state energy discussed before.

\mathcal{F} may again be evaluated, when H is given in the harmonic approximation by Eqs. (1.1.3), (1.1.4), by diagonalizing H in terms of the normal modes. But it should be remembered that the linear terms in the expansion of the interatomic potential were zero since the expansion was about the equilibrium, *static*, configuration of the atoms. As the system is heated up, the lattice will in general expand and the equilibrium atomic spacing will change with temperature. This leads to a change in the harmonic frequencies of the normal modes. However, we will stick to an expansion about the static equilibrium configuration at $T = 0$ (neglecting zero-point vibrations), and remain in the idealized harmonic approximation for which, in the absence of anharmonic corrections, the thermal expansion does not occur.

The direct way to evaluate Eq. (2.1.6) is to perform the trace directly over the eigenstates of the set of normal mode oscillators whose frequencies are given by Eq. (1.1.11). To construct these eigenstates we need to generalize the creation and annihilation operators given in Eq. (1.5.3) for the single vibrating atom to the normal mode case. The main complication is that the normal mode displacement operators

$$Q_{\mathbf{k}}(t) = \sqrt{\left(\frac{M}{N} \right)} \sum_i e^{i\mathbf{k} \cdot \mathbf{R}_i} u_i \quad (2.1.7)$$

are now complex and, using the fact that the atomic displacements u_i are real, have to satisfy the reality condition

$$Q_{\mathbf{k}}^* = Q_{-\mathbf{k}} \quad (2.1.8)$$

obtained by taking the conjugate of (2.1.7). Eq. (2.1.8) means that the modes \mathbf{k} and $-\mathbf{k}$ are not in fact independent dynamical variables. The definition (2.1.7) may be inverted by writing

$$u_i = \frac{1}{\sqrt{(NM)}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_i} Q_{\mathbf{k}}, \quad (2.1.9)$$

which follows from (2.1.7) on using periodic boundary conditions.

Inserting (2.1.7), and the analogous definition of the normal mode momentum variable $P_{\mathbf{k}}$,

$$P_{\mathbf{k}} = \frac{1}{\sqrt{(NM)}} \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} p_i, \quad (2.1.10)$$

into the hamiltonian (1.1.3), (1.1.6), and using the normal mode frequencies (1.1.11), the hamiltonian may be rewritten as

$$H = \frac{1}{2} \sum_{\mathbf{k}} (P_{\mathbf{k}}P_{-\mathbf{k}} + \Omega_{\mathbf{k}}^2 Q_{\mathbf{k}}Q_{-\mathbf{k}}). \quad (2.1.11)$$

From Eq. (2.1.7) the commutation rules are

$$[P_{\mathbf{k}}, Q_{\mathbf{k}'}] = -i\delta_{\mathbf{k},-\mathbf{k}'}, \quad (2.1.12)$$

and annihilation and creation operators may be introduced as in Eq. (1.5.3) by the relations [using (2.1.8)]

$$b_{\mathbf{k}} = \frac{1}{\sqrt{(2\Omega_{\mathbf{k}})}} (Q_{\mathbf{k}} + iP_{\mathbf{k}}), \quad b_{\mathbf{k}}^\dagger = \sqrt{\left(\frac{\Omega_{\mathbf{k}}}{2}\right)} (Q_{-\mathbf{k}} - iP_{-\mathbf{k}}), \quad (2.1.13)$$

from which

$$[b_{\mathbf{k}}, b_{\mathbf{k}'}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'}, \quad (2.1.14)$$

and H may be re-expressed as

$$H = \sum_{\mathbf{k}} \Omega_{\mathbf{k}} (b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \frac{1}{2}). \quad (2.1.15)$$

The normalized, n -phonon eigenstates may be written (see Appendix 1)

$$|n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots\rangle = \prod_{\mathbf{k}} \frac{(b_{\mathbf{k}}^\dagger)^{n_{\mathbf{k}}}}{\sqrt{(n_{\mathbf{k}}!)}} |0\rangle, \quad (2.1.16)$$

where $|0\rangle$ is the ground state, defined by

$$b_{\mathbf{k}}|0\rangle = 0 \quad (2.1.17)$$

for all \mathbf{k} . It may be shown then that $b_{\mathbf{k}}^\dagger b_{\mathbf{k}}$ is the phonon number operator for phonons with wave-vector \mathbf{k}

$$b_{\mathbf{k}}^\dagger b_{\mathbf{k}} |n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots\rangle = n_{\mathbf{k}} |n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots\rangle. \quad (2.1.18)$$

Hence, using the fact that the $b_{\mathbf{k}}$'s commute for different \mathbf{k} ,

$$\langle n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots | e^{-\beta H} | n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots \rangle = e^{-\beta \sum_{\mathbf{k}} \Omega_{\mathbf{k}} (n_{\mathbf{k}} + \frac{1}{2})}, \quad (2.1.19)$$

and the free energy is given by

$$\begin{aligned} \mathcal{F} &= -\frac{1}{\beta} \log \sum_{\{n_{\mathbf{k}}\}} e^{-\beta \sum_{\mathbf{k}} \Omega_{\mathbf{k}} (n_{\mathbf{k}} + \frac{1}{2})} \\ &= -\frac{1}{\beta} \log \sum_{\{n_{\mathbf{k}}\}} \prod_{\mathbf{k}} e^{-\beta \Omega_{\mathbf{k}} (n_{\mathbf{k}} + \frac{1}{2})}. \end{aligned} \quad (2.1.20)$$

Here $\{n_{\mathbf{k}}\}$ indicates the set of choices of $n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots$, where each $n_{\mathbf{k}}$ can take all integer values. Inverting sum and product we have, for fixed \mathbf{k} ,

$$\sum_{n_{\mathbf{k}}=0,1,2,\dots} e^{-\beta \Omega_{\mathbf{k}} (n_{\mathbf{k}} + \frac{1}{2})} = \frac{e^{-\frac{1}{2}\beta \Omega_{\mathbf{k}}}}{1 - e^{-\beta \Omega_{\mathbf{k}}}} = \{2 \sinh(\frac{1}{2}\beta \Omega_{\mathbf{k}})\}^{-1},$$

and hence we obtain the well-known result

$$\mathcal{F} = \frac{1}{\beta} \sum_{\mathbf{k}} \log \{2 \sinh(\frac{1}{2}\beta \Omega_{\mathbf{k}})\}. \quad (2.1.21)$$

At zero temperature ($\beta \rightarrow \infty$) this reduces to the ground state energy, Eq. (1.1.12),

$$\mathcal{F} \rightarrow \frac{1}{2} \sum_{\mathbf{k}} \Omega_{\mathbf{k}} \quad \text{as} \quad \beta \rightarrow \infty. \quad (2.1.22)$$

2.2. THE PHONON TEMPERATURE GREEN'S FUNCTION

As in the previous chapter, another way of calculating the free energy is by integration of the average interaction energy over the coupling constant. Again, this is not really necessary for the harmonic lattice, for which the method of Sec. 2.1 provides the straightforward solution. However, as in the zero-temperature case the more general approach provides a powerful systematic method for dealing with more complicated many-body problems such as the anharmonic lattice. Here we apply the method to the harmonic lattice at non-zero temperatures in order to provide a simple illustration of the technique.

We begin by generalizing the formula (1.2.3), which expresses the ground state energy as an integral over coupling constant, to the free energy (2.1.6). Let $|\Psi_n(\lambda)\rangle$, $E_n(\lambda)$ be the exact eigenfunctions and eigenvalues of the hamiltonian $H(\lambda)$ of Eq. (1.1.5) with variable coupling constant. Then

$$-\beta\mathcal{F} = \log \sum_n e^{-\beta E_n(\lambda)},$$

and, since $\partial E_n(\lambda)/\partial\lambda = \langle\Psi_n(\lambda)|H_1|\Psi_n(\lambda)\rangle$ [compare Eq. (1.2.2)], we have

$$\frac{\partial\mathcal{F}}{\partial\lambda} = \frac{\sum_n e^{-\beta E_n} \langle\Psi_n(\lambda)|H_1|\Psi_n(\lambda)\rangle}{\sum_n e^{-\beta E_n}} = \langle H_1 \rangle_\lambda, \quad (2.2.1)$$

where $\langle \cdots \rangle_\lambda$ now denotes the *thermal average*

$$\langle H_1 \rangle_\lambda = \text{Tr}\{e^{-\beta H(\lambda)} H_1\} / \text{Tr} e^{-\beta H(\lambda)}. \quad (2.2.2)$$

Thus for the harmonic lattice case we have, instead of the expression (1.2.4) for ΔE_G ,

$$\Delta\mathcal{F} = \frac{1}{2}M \sum_{i \neq j} D_{ij} \int_0^1 d\lambda \langle u_i u_j \rangle_\lambda, \quad (2.2.3)$$

where $\Delta\mathcal{F}$ is the change in free energy as λ is switched on.

To calculate thermal averages such as that in Eq. (2.2.3) (other examples will be encountered later) we define a *single-particle temperature Green's function* by

$$G_{ij}(\sigma - \sigma') = \langle T[\tilde{u}_i(\sigma)\tilde{u}_j(\sigma')] \rangle. \quad (2.2.4)$$

The brackets $\langle \cdot \cdot \cdot \rangle$ now denote the thermal average, defined as in Eq. (2.2.2), of the operator product at inverse temperature β , and the time variable in the argument of the operators has been replaced by a "temperature variable" σ . $\tilde{u}(\sigma)$ is a modified Heisenberg operator in the variable σ ,

$$\tilde{u}(\sigma) = e^{\sigma H} u e^{-\sigma H}, \quad (2.2.5)$$

which satisfies the temperature analog of the Schrödinger equation, the *Bloch equation* [Bloch (1932)]

$$\frac{\partial \tilde{u}(\sigma)}{\partial \sigma} = [H, \tilde{u}]. \quad (2.2.6)$$

The T symbol orders the operators according to the value of σ with the larger on the left. The temperature Green's function is a function of the variables σ and σ' and, if H is independent of time, it depends only on the difference $\sigma - \sigma'$ (this follows, as at $T = 0$, from the analysis of Appendix 2).

It will be noted that Eqs. (2.2.5) and (2.2.6) can be obtained formally from the conventional time-dependent Heisenberg picture by replacing it by σ . σ may thus be called an *imaginary time* variable. By regarding σ as a complex variable which can take real and imaginary values, one can thus establish a correspondence between the Green's function methods at finite and at zero temperatures, and also between temperature and real-time Green's functions at finite T (see Appendix 2). This correspondence will become apparent as the analysis proceeds.

The thermal average required for the free energy may now be expressed in terms of G_{ij} by

$$\langle u_i u_j \rangle = \lim_{\sigma \rightarrow 0^+} G_{ij}(\sigma). \quad (2.2.7)$$

It is understood here that H contains the coupling constant λ .

The calculation of G now proceeds in close analogy with the zero temperature case. The equation of motion with respect to the temperature variable σ follows, by the same analysis as led to Eq. (1.4.14), as

$$\left(\frac{d^2}{d\sigma^2} - \Omega_0^2 \right) G_{ij}(\sigma) = -\frac{1}{M} \delta_{ij} \delta(\sigma) + \lambda \sum_l D_{il} G_{lj}(\sigma). \quad (2.2.8)$$

We shall again solve this by a Fourier transform method. First we need to examine the analytic form of the unperturbed Green's function

$G^0(\sigma)\delta_{ij}$. Introducing the creation operator for the atom with displacement u_i as in Eq. (1.5.3), we find

$$B_i(\sigma) = e^{-\Omega_0\sigma}B_i, \quad B_i^\dagger(\sigma) = e^{+\Omega_0\sigma}B_i^\dagger, \quad (2.2.9)$$

so that

$$G^0(\sigma) = \frac{1}{2M\Omega_0} \langle T[(e^{-\Omega_0\sigma}B_i + e^{+\Omega_0\sigma}B_i^\dagger)(B_i + B_i^\dagger)] \rangle. \quad (2.2.10)$$

[Note that, for real σ , the operator $B_i^\dagger(\sigma)$ is *not* the adjoint of $B_i(\sigma)$. The notation should not lead to any confusion.]

It is convenient to define

$$\left. \begin{aligned} G^{0>}(\sigma) &= G^0(\sigma) & (\sigma > 0), \\ G^{0<}(\sigma) &= G^0(\sigma) & (\sigma < 0). \end{aligned} \right\} \quad (2.2.11)$$

Using the fact that $B^\dagger B$ is a number operator for phonons of constant frequency Ω_0 , we have

$$\langle B_i^\dagger B_i \rangle = n_0 = 1/(e^{\beta\Omega_0} - 1), \quad (2.2.12)$$

where n_0 is the Planck function (the distribution function for the phonons at inverse temperature β), and

$$\langle B_i B_i^\dagger \rangle = n_0 + 1 = 1/(1 - e^{-\beta\Omega_0}). \quad (2.2.13)$$

Hence

$$G^{0>}(\sigma) = \frac{1}{2M\Omega_0} \{(n_0 + 1) e^{-\Omega_0\sigma} + n_0 e^{+\Omega_0\sigma}\},$$

and

$$G^{0<}(\sigma) = \frac{1}{2M\Omega_0} \{n_0 e^{-\Omega_0\sigma} + (n_0 + 1) e^{+\Omega_0\sigma}\},$$

from which, for all σ ,

$$G^0(\sigma) = \frac{1}{2M\Omega_0} \{(n_0 + 1) e^{-\Omega_0|\sigma|} + n_0 e^{+\Omega_0|\sigma|}\}. \quad (2.2.14)$$

It will be seen that $G^{0>}$ and $G^{0<}$ both contain the real exponentials $\exp(-\Omega_0\sigma)$ and $\exp(+\Omega_0\sigma)$. If we want to make a Fourier transform of G^0 , the integrals involved will now diverge exponentially at the limits $\sigma \rightarrow \pm\infty$. However, if we restrict ourselves to the region $0 \leq \sigma \leq \beta$, it may be seen that the term $\exp(\beta\Omega_0)$ in the denominator of the Planck

function will cancel the exponential growth of the $\exp(\sigma\Omega_0)$ in the numerator, thus keeping the integrand finite for any value of β . This argument suggests that convergence problems will be overcome provided the Fourier transforms are made over this finite region of the σ axis. We therefore artificially repeat the function periodically in the regions $0 \leq \sigma \leq \beta$, $\beta \leq \sigma \leq 2\beta$ etc. Thus the function $G^0(\sigma)$ can be represented over the region $0 \leq \sigma \leq \beta$ by means of a *Fourier series* of the form [Abrikosov, Gor'kov, and Dzyaloshinskii (1959), Fradkin (1959), Martin and Schwinger (1959)]

$$G^0(\sigma) = \sum_{\mu} e^{2\pi i \mu \sigma / \beta} G^0(\mu), \quad (2.2.15)$$

where μ takes integer values $0, \pm 1, \pm 2, \dots$. In fact one can prove directly (see Appendix 2) that the single-particle temperature Green's function $G(\sigma)$ for bosons is always periodic in σ with period β , for σ in the range $0 \leq \sigma \leq \beta$. [It is left to the reader to check this property for the function (2.2.14). For fermions the corresponding Green's function is antiperiodic with period β , and therefore periodic over the range 2β .]

By Fourier's theorem Eq. (2.2.15) may be inverted to give

$$G^0(\bar{\mu}) = \frac{1}{\beta} \int_0^{\beta} d\sigma e^{-i\bar{\mu}\sigma} G^0(\sigma), \quad (2.2.16)$$

where

$$\bar{\mu} = 2\mu\pi/\beta. \quad (2.2.17)$$

The Fourier coefficient $G^0(\bar{\mu})$, which replaces the Fourier transform $G^0(\omega)$ of the zero-temperature theory, is thus a function of a discrete frequency variable $\bar{\mu}$. For fermions there is a corresponding Fourier expansion with $\bar{\mu} = (2\mu + 1)\pi/\beta$. Using the fact that

$$\begin{aligned} \frac{1}{\beta} \int_0^{\beta} d\sigma e^{-i\bar{\mu}\sigma} e^{-\Omega_0\sigma} (n_0 + 1) &= \frac{1}{\beta} \frac{(e^{-\beta\Omega_0} - 1)}{-i\bar{\mu} - \Omega_0} (n_0 + 1) \\ &= \frac{1/\beta}{i\bar{\mu} + \Omega_0}, \end{aligned} \quad (2.2.18)$$

we thus find, substituting (2.2.14) into (2.2.16),

$$\begin{aligned} G^0(\bar{\mu}) &= \frac{1}{2\Omega_0\beta M} \left\{ \frac{1}{i\bar{\mu} + \Omega_0} - \frac{1}{i\bar{\mu} - \Omega_0} \right\} \\ &= \frac{1}{\beta M} \frac{1}{\bar{\mu}^2 + \Omega_0^2}. \end{aligned} \quad (2.2.19)$$

The same result could also have been obtained from the equation of motion (2.2.8), by inserting the Fourier expansion (2.2.15) in the limit $\lambda = 0$ and using a Fourier series representation of the δ -function.

It is seen that $G^0(\bar{\mu})$ is a similar function to the zero-temperature Fourier transform $G^0(\omega)$, Eq. (1.6.9), with two poles corresponding to imaginary values of $\bar{\mu}$ at $i\bar{\mu} = \pm\Omega_0$. We obtained this simple result because we worked with a Green's function defined in terms of imaginary time variables. It is a consequence of the periodicity property of this Green's function, which permitted the Fourier series expansion (2.2.15). The *real-time* Green's function $G^0(t)$ at finite temperature T , defined as the thermal average of

$$-iT[\bar{u}_i(t)\bar{u}_i(0)]$$

for $\lambda = 0$, has evidently the same form as $G^0(\sigma)$, with $|\sigma|$ replaced by $i|t|$, but its Fourier transform $G^0(\omega)$ is a more complicated function than at $T = 0$ and still involves the Planck distribution functions n_0 and $(n_0 + 1)$. The real-time functions are discussed in Sec. 2.3 below.

The solution of the equation of motion (2.2.8) for $\lambda \neq 0$ now follows directly from the equation

$$G_{ij}(\bar{\mu}) = G^0(\bar{\mu})\delta_{ij} - \lambda\beta M G^0(\bar{\mu}) \sum_l D_{il} G_{lj}(\bar{\mu}), \quad (2.2.20)$$

which corresponds to the Fourier-transformed integral equation (1.6.2). This is solved, as in the zero-temperature case of Eq. (1.6.6), in terms of k -space Green's functions as

$$\begin{aligned} G_{\mathbf{k}}(\bar{\mu}) &= \frac{G^0(\bar{\mu})}{1 + \lambda\beta M G^0(\bar{\mu}) D_{\mathbf{k}}} \\ &= \frac{1/\beta M}{\bar{\mu}^2 + \Omega_{\mathbf{k}}^2}, \end{aligned} \quad (2.2.21)$$

where $\Omega_{\mathbf{k}}^2 = \Omega_0^2 + \lambda D_{\mathbf{k}}$ as before. Thus the effect of the interaction is again to shift the poles of the Green's function from $\pm\Omega_0$ to $\pm\Omega_{\mathbf{k}}$.

Finally, the expression (2.2.3), (2.2.7) for the change in free energy may be expressed in terms of $G_{\mathbf{k}}(\bar{\mu})$:

$$\Delta \mathcal{F} = \frac{1}{2} \frac{M}{N} \sum_{i \neq j} D_{ij} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \int_0^1 d\lambda \lim_{\sigma \rightarrow 0^+} \sum_{\bar{\mu}} e^{i\bar{\mu}\sigma} G_{\mathbf{k}}(\bar{\mu}), \quad (2.2.22)$$

leading to

$$\Delta \mathcal{F} = \lim_{\sigma \rightarrow 0^+} \frac{1}{2} M \int_0^1 d\lambda \sum_{\mathbf{k}} D_{\mathbf{k}} \sum_{\bar{\mu}} e^{i\bar{\mu}\sigma} G_{\mathbf{k}}(\bar{\mu}). \quad (2.2.23)$$

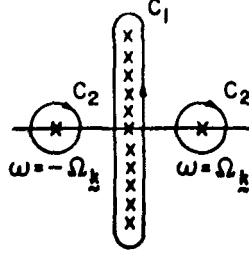


Fig. 2.1. Contours for the evaluation of $G_{\mathbf{k}}^>(\sigma)$.

For $\sigma > 0$ the function

$$\sum_{\bar{\mu}} e^{i\bar{\mu}\sigma} G_{\mathbf{k}}(\bar{\mu})$$

is $G_{\mathbf{k}}^>(\sigma)$, and in order to perform the frequency sum over $\bar{\mu}$ it is convenient to introduce a contour integral representation

$$G_{\mathbf{k}}^>(\sigma) = \frac{\beta}{2\pi i} \int_{C_1} d\omega \frac{e^{\sigma\omega}}{e^{\beta\omega} - 1} G_{\mathbf{k}}(i\omega), \quad (2.2.24)$$

where C_1 is the contour in the complex ω -plane encircling the poles of $1/(e^{\beta\omega} - 1)$ which lie on the imaginary axis at $\omega = 2\pi i\mu/\beta$ ($\mu = 0, \pm 1, \pm 2, \dots$) (Fig. 2.1). Because of the fact that $0 \leq \sigma \leq \beta$, the $e^{\sigma\omega}$ in the integrand does not lead to any divergence, and if Eq. (2.2.24) is evaluated by residues, it is seen that the contour integral leads to the Fourier series for

$G_{\mathbf{k}}^>(\sigma)$. Now

$$G_{\mathbf{k}}(i\omega) = \frac{1/\beta M}{-\omega^2 + \Omega_{\mathbf{k}}^2},$$

and we can obtain (2.2.24) in closed form by deforming the contour C_1 to a contour C_2 encircling the poles $\omega = \pm\Omega_{\mathbf{k}}$ of $G_{\mathbf{k}}(i\omega)$ in the negative sense. (The integrals over the large arcs involved in the deformation vanish.) We now use the residue theorem again, evaluating the contributions of the two poles which lie inside C_2 , to obtain in the limit $\sigma \rightarrow 0+$

$$\begin{aligned} G_{\mathbf{k}}(\sigma = 0+) &= \frac{1}{2\Omega_{\mathbf{k}}M} \left\{ \frac{1}{e^{\beta\Omega_{\mathbf{k}}} - 1} + \frac{1}{1 - e^{-\beta\Omega_{\mathbf{k}}}} \right\} \\ &= \frac{1}{2\Omega_{\mathbf{k}}M} \coth \left(\frac{1}{2}\beta\Omega_{\mathbf{k}} \right). \end{aligned} \quad (2.2.25)$$

But by direct differentiation with respect to λ it may be seen that

$$\frac{\partial}{\partial \lambda} \log \left\{ \sinh \frac{\beta\Omega_{\mathbf{k}}(\lambda)}{2} \right\} = \frac{\beta D_{\mathbf{k}}}{4\Omega_{\mathbf{k}}} \coth \left(\frac{1}{2}\beta\Omega_{\mathbf{k}} \right). \quad (2.2.26)$$

Hence Eq. (2.2.23) reduces to

$$\begin{aligned} \Delta \mathcal{F} &= \frac{1}{2}M \int_0^1 d\lambda \sum_{\mathbf{k}} D_{\mathbf{k}} G_{\mathbf{k}}(\sigma = 0+) \\ &= \frac{1}{\beta} \sum_{\mathbf{k}} \log \left\{ \frac{\sinh \left(\frac{1}{2}\beta\Omega_{\mathbf{k}} \right)}{\sinh \left(\frac{1}{2}\beta\Omega_0 \right)} \right\}, \end{aligned} \quad (2.2.27)$$

which is in precise agreement with the result obtained by direct calculation for the change in the free energy on switching on λ .

From this example we see that there are close analogies between the time-dependent Green's function at $T = 0$ and the temperature Green's function at finite T . The main difference is that the imaginary time variable it has become transformed to a real temperature variable σ , and that σ is to be confined to a restricted range of values $0 \leq \sigma \leq \beta$. This analogy will be further exploited in the following chapter.

2.3. THE REAL-TIME GREEN'S FUNCTION AND NEUTRON SCATTERING AT FINITE TEMPERATURES

The temperature Green's function studied in the last section enabled us to calculate equilibrium thermodynamic properties which are independent of the time. To study excitations, however, we need to be able to calculate time-dependent correlation functions, and for this we require the finite-temperature generalization of the real-time Green's function studied in Chap. 1. As an example of such a quantity we now consider the generalization to non-zero temperatures of the neutron scattering cross-section evaluated for $T = 0$ in Sec. 1.7.

At $T \neq 0$ we cannot assume in calculating the cross-section that the target is in its ground state initially but have to consider a distribution of initial states $|\psi_I\rangle$ with energy E_I , occupied with probability p_I . The generalization of the formula (1.3.10) for the differential cross-section is thus

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{K'}{2\pi K} \left(\frac{M}{2\pi}\right)^2 |V_{\mathbf{q}}|^2 \sum_I \int_{-\infty}^{\infty} e^{i\omega t} dt \sum_{j\ell} p_I \times \langle \psi_I | e^{-i\mathbf{q} \cdot \tilde{\mathbf{X}}_j(t)} e^{i\mathbf{q} \cdot \tilde{\mathbf{X}}_{\ell}(0)} | \psi_I \rangle. \quad (2.3.1)$$

For a canonical ensemble at inverse temperature β ,

$$p_I = e^{-\beta E_I} / \sum_I e^{-\beta E_I}, \quad (2.3.2)$$

and thus the cross-section now involves a thermal average over the ensemble. We deduce that the correlation function (1.3.11), (1.3.12) is replaced by

$$F(\mathbf{q}, t) = \sum_{j\ell} e^{i\mathbf{q} \cdot (\mathbf{R}_I - \mathbf{R}_j)} \langle e^{-i\mathbf{q} \cdot \tilde{\mathbf{u}}_j(t)} e^{i\mathbf{q} \cdot \tilde{\mathbf{u}}_{\ell}(0)} \rangle \simeq q^2 \sum_{j\ell} e^{i\mathbf{q} \cdot (\mathbf{R}_I - \mathbf{R}_j)} \langle \tilde{\mathbf{u}}_j(t) \tilde{\mathbf{u}}_{\ell}(0) \rangle, \quad (2.3.3)$$

where the brackets now denote a thermal average of the time-dependent quantities enclosed. (The Debye-Waller factor—now temperature-dependent—has again been omitted.)

Again, for the present problem this correlation function can be obtained directly from the exact phonon eigenstates. To obtain it by a

Green's function method, we define the single-particle real-time Green's function at temperature T as

$$G_{ij}(t - t') = -i \langle T[\tilde{u}_i(t)\tilde{u}_j(t')] \rangle, \quad (2.3.4)$$

which is an immediate generalization of the zero-temperature definition (1.4.6). The only difference is in the meaning of the brackets: the ground state expectation value has been replaced by a thermal average

$$\langle \mathcal{O} \rangle = \text{Tr} (e^{-\beta H} \mathcal{O}) / \text{Tr} e^{-\beta H}. \quad (2.3.5)$$

$\tilde{u}(t)$ is a time-dependent Heisenberg operator as in Chap. 1. The Green's function (2.3.4) is thus a function of both temperature and time variables.

To obtain $G_{ij}(t)$ we again appeal to the analogy between the time-dependent and the temperature formalism. It is shown in Appendix 2 that the time-dependent Green's function at temperature T can be obtained by an *analytic continuation* of the temperature Green's function. For this purpose it is in fact simpler to work not with the time-ordered but with the *retarded* Green's function at temperature T

$$G_{ij}^R(t - t') = -i\theta(t - t') \langle [\tilde{u}_i(t), \tilde{u}_j(t')] \rangle. \quad (2.3.6)$$

The essential formulae are Eqs. (A.2.8), (A.2.22) of Appendix 2:

$$G_{ij}^R(\omega) = \int_{-\infty}^{\infty} (1 - e^{-\beta\omega'}) \frac{J_{ij}(\omega')}{\omega - \omega' + i\eta} \frac{d\omega'}{2\pi} \quad (\eta = 0+), \quad (2.3.7)$$

$$G_{ij}(\bar{\mu}) = -\frac{1}{\beta} \int_{-\infty}^{\infty} (1 - e^{-\beta\omega'}) \frac{J_{ij}(\omega')}{-i\bar{\mu} - \omega'} \frac{d\omega'}{2\pi}, \quad (2.3.8)$$

which express the Fourier transform of $G_{ij}^R(t)$ and the Fourier coefficient in the Fourier series for $G_{ij}(\sigma)$ in terms of the Fourier transform

$$J_{ij}(\omega) = \int_{-\infty}^{\infty} \langle \tilde{u}_i(t)\tilde{u}_j(0) \rangle e^{i\omega t} dt \quad (2.3.9)$$

of the time-correlation function $\langle \tilde{u}_i(t)\tilde{u}_j(0) \rangle$.

Eqs. (2.3.7), (2.3.8) apply equally to the \mathbf{k} -space Green's functions, and we see that we obtain $G_{\mathbf{k}}^R(\omega)$ by replacing $-i\bar{\mu}$ in $-\beta G_{\mathbf{k}}(\bar{\mu})$,

Eq. (2.2.21), by $\omega + i\eta$, leading at once to

$$\begin{aligned} G_{\mathbf{k}}^R(\omega) &= -\frac{1}{M} \frac{1}{-(\omega + i\eta)^2 + \Omega_{\mathbf{k}}^2} \\ &= \frac{1}{2M\Omega_{\mathbf{k}}} \left\{ \frac{1}{\omega - \Omega_{\mathbf{k}} + i\eta} - \frac{1}{\omega + \Omega_{\mathbf{k}} + i\eta} \right\}. \end{aligned} \quad (2.3.10)$$

We can invert the relation between $G_{\mathbf{k}}^R(\omega)$ and $J_{\mathbf{k}}(\omega)$ to obtain $J_{\mathbf{k}}(\omega)$ explicitly, using the formula [Messiah (1961, p. 469)] for the real and imaginary parts of the singular function $(x + i\eta)^{-1}$:

$$\frac{1}{x + i\eta} = \mathcal{P} \frac{1}{x} - i\pi\delta(x) \quad (\eta = 0+), \quad (2.3.11)$$

where \mathcal{P} denotes the principal part. For $J_{\mathbf{k}}(\omega)$ real, we thus have from Eqs. (2.3.7) and (2.3.10)

$$\begin{aligned} J_{\mathbf{k}}(\omega) &= -\frac{2}{1 - e^{-\beta\omega}} \text{Im } G_{\mathbf{k}}^R(\omega) \\ &= \frac{\pi}{M\Omega_{\mathbf{k}}(1 - e^{-\beta\omega})} \{ \delta(\omega - \Omega_{\mathbf{k}}) - \delta(\omega + \Omega_{\mathbf{k}}) \}. \end{aligned} \quad (2.3.12)$$

The δ -function peaks in the *spectral density function* $J_{\mathbf{k}}(\omega)$ correspond to the poles at $\pm\Omega_{\mathbf{k}}$ of the retarded Green's function.

The lattice function corresponding to $J_{\mathbf{k}}(\omega)$ is

$$J_{ij}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} J_{\mathbf{k}}(\omega) e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}, \quad (2.3.13)$$

and we finally obtain the time correlation function (2.3.3) by inverting the Fourier transform (2.3.9). Thus

$$F(\mathbf{q}, t) = q^2 \sum_{j'l} e^{i\mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_j)} \int_{-\infty}^{\infty} J_{j'l}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi},$$

and, substituting (2.3.13) and (2.3.12), we can perform the frequency integral to obtain the final result

$$\begin{aligned} F(\mathbf{q}, t) &= \frac{q^2}{2NM} \sum_{j'l} \sum_{\mathbf{k}} \frac{1}{\Omega_{\mathbf{k}}} \{ (n_{\mathbf{k}} + 1) e^{-i\Omega_{\mathbf{k}} t} e^{i(\mathbf{q} - \mathbf{k}) \cdot (\mathbf{R}_l - \mathbf{R}_j)} \\ &\quad + n_{\mathbf{k}} e^{i\Omega_{\mathbf{k}} t} e^{i(\mathbf{q} + \mathbf{k}) \cdot (\mathbf{R}_l - \mathbf{R}_j)} \}. \end{aligned} \quad (2.3.14)$$

Here

$$n_{\mathbf{k}} = \frac{1}{e^{\beta\Omega_{\mathbf{k}}} - 1} \quad (2.3.15)$$

is the distribution function for phonons of wave-vector \mathbf{k} , and we have changed the sign of \mathbf{k} in the second term.

Eq. (2.3.14) is the finite-temperature generalization of Eq. (1.7.3) and gives the temperature dependence of the neutron scattering cross-section. We see that $F(\mathbf{q}, t)$ now contains, in addition to the phonon emission processes described by the first term, phonon absorption processes described by the second term in which the target loses energy $\hbar\Omega_{\mathbf{k}}$ to the neutron. As the temperature is increased these absorption processes become more important until, when the temperature is large compared with the phonon frequencies, there is equipartition and emission and absorption processes are then equally frequent.

For completeness we finally use Eqs. (A.2.9) and (A.2.11) of Appendix 2 to evaluate the time-ordered real-time Green's function for the phonon problem at temperature T . (The details are left to the reader.) The Fourier transform $G_{\mathbf{k}}(\omega)$ is given by

$$G_{\mathbf{k}}(\omega) = -\frac{n_{\mathbf{k}} + 1}{2M\Omega_{\mathbf{k}}} \left\{ \frac{1}{\omega + \Omega_{\mathbf{k}} - i\eta} - \frac{1}{\omega - \Omega_{\mathbf{k}} + i\eta} \right\} - \frac{n_{\mathbf{k}}}{2M\Omega_{\mathbf{k}}} \left\{ \frac{1}{\omega - \Omega_{\mathbf{k}} - i\eta} - \frac{1}{\omega + \Omega_{\mathbf{k}} + i\eta} \right\}. \quad (2.3.16)$$

The poles of this function now correspond to the energy differences between the excited states of the system. In fact, because in the harmonic approximation the matrix elements governing transitions between phonon states vanish unless only a single phonon is emitted or absorbed, the poles are at $\pm\Omega_{\mathbf{k}}$ as at $T = 0$ (but there are now two poles in the upper and two in the lower half-plane). In more general problems the function $G(\omega)$ contains both energies and lifetimes of excited states. Eq. (2.3.16) should be compared with the simpler expressions for $G_{\mathbf{k}}(\bar{\mu})$, Eq. (2.2.21), and $G_{\mathbf{k}}^R(\omega)$, Eq. (2.3.10); we note that, as at $T = 0$, the retarded Green's function is regular in the upper half of the ω -plane. The time-dependent Green's function corresponding to Eq. (2.3.16) is

$$G_{\mathbf{k}}(t) = -\frac{i}{2M\Omega_{\mathbf{k}}} (n_{\mathbf{k}} + 1) e^{-i\Omega_{\mathbf{k}}|t|} - \frac{i}{2M\Omega_{\mathbf{k}}} n_{\mathbf{k}} e^{i\Omega_{\mathbf{k}}|t|}, \quad (2.3.17)$$

in close analogy to the form of the temperature Green's function [compare Eq. (2.2.14)].