



# SURFACE EXCITATIONS

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We dedicate this volume to the memory of the outstanding Soviet condensed matter theorist, Ilya Mihailovich Lifshitz, who died on October 23, 1982. His work during the past forty years pointed to new directions in many areas of condensed matter physics, including low temperature physics, metal physics, the dynamical properties of crystals containing defects and of disordered crystals, and polymer physics. It is particularly fitting that a volume concerned with surface excitations is dedicated to Ilya Mihailovich, whose pioneering work with Rosenzweig in the late 1940's laid the foundations for the present day theory of the vibrations of crystal surfaces. A man of vast heart, great kindness, and unusual generosity, Ilya Mihailovich will be missed by his colleagues on the International Advisory Board of this series, and by all who had the good fortune to know him.

V.M. Agranovich  
R. Loudon  
A.A. Maradudin

*Oh, how many of them there  
are in the fields!  
But each flowers in its  
own way —  
In this is the highest achievement  
of a flower!*

*Matsuo Bashō  
1644 – 1694*

## PREFACE TO THE SERIES

“Modern Problems in Condensed Matter Sciences” is a series of contributed volumes and monographs on condensed matter science that is published by North-Holland Publishing Company. This vast area of physics is developing rapidly at the present time, and the numerous fundamental results in it define to a significant degree the face of contemporary science. This being so, it is clear that the most important results and directions for future developments can only be covered by an international group of authors working in cooperation.

Both Soviet and Western scholars are taking part in the series, and each contributed volume has, correspondingly, two editors. Furthermore, it is intended that the volumes in the series will be published subsequently in Russian by the publishing house “Nauka”.

The idea for the series and for its present structure was born during discussions that took place in the USSR and the USA between the former President of North-Holland Publishing Company, Drs. W.H. Wimmers, and the General Editors.

The establishment of this series of books, which should become a distinguished encyclopedia of condensed matter science, is not the only important outcome of these discussions. A significant development is also the emergence of a rather interesting and fruitful form of collaboration among scholars from different countries. We are deeply convinced that such international collaboration in the spheres of science and art, as well as other socially useful spheres of human activity, will assist in the establishment of a climate of confidence and peace.

The General Editors of the Series,

V.M. Agranovich

A.A. Maradudin

## PREFACE

This volume presents articles on the main kinds of surface excitation supported by solids and liquids. In most cases, the excitations considered are surface versions of excitations that also occur in the bulk material. Surface excitations often display a richer variety of phenomena than their bulk counterparts. They can be much more difficult to observe experimentally, and their theoretical treatment generally requires extensions of the methods used in the bulk. For these reasons, the study of surface excitations remains an advancing field of research in cases where the corresponding bulk studies have become somewhat routine.

The articles presented in this volume span a wide range of interest, from the important practical applications to device technology that have provided a strong stimulus for work on surface vibrations, to the developments in linear response theory that have been generated by the need to include surfaces in the formalism. The majority of the articles are concerned with the varieties of surface excitation that occur on solids, including vibrational, magnetic, and electronic. The surface excitations on liquids are somewhat less varied, but a final article on this case is included since there are interesting similarities and contrasts with the corresponding excitations on solids.

It should finally be mentioned that we have not provided a separate article on surface polaritons since this topic is very fully covered in Volume 1 of the present series (Surface Polaritons, edited by V.M. Agranovich and D.L. Mills, North-Holland, 1982).

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# Surface Linear Response Functions

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*Edited by*

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## *1. Introduction*

Linear response theory is well established as a technique for investigating the spectrum of excitations in solids and fluids. The method essentially involves calculating the response of a system to a small applied stimulus. The results may be expressed in terms of response functions, which can be directly related to quantum mechanical Green's functions. As well as providing information about the dispersion relation of any excitation, the response functions enable one to deduce the power spectrum of the thermally excited fluctuations in the excitation amplitude. This is achieved by application of the fluctuation-dissipation theorem (or generalized Nyquist theorem), which relates the mean square fluctuations in the excitation amplitude to the imaginary part of an appropriately defined response function. General accounts of the linear response method have been given, for example, by Landau and Lifshitz (1969), Kubo (1966), Barker and Loudon (1972) and Forster (1975).

The purpose of this chapter is to describe how linear response theory can be applied to solids and fluids with restricted geometries. It is well known that the existence of a surface can give rise to localized surface excitations (e.g. surface magnons or surface phonons). These occur as a consequence of the lack of translational invariance of the system in the direction perpendicular to the surface. The surface excitations are characterized by a wave-like behavior of the excitation amplitude for propagation parallel to the surface (since the system is still translationally invariant in this direction), but the amplitude decays with distance away from the surface. By contrast the bulk excitations, which are the only excitations occurring in an effectively infinite system, are wave-like in three dimensions, having a constant amplitude but varying phase. The bulk excitations are also influenced by the presence of a surface, since they can in general be reflected back from the surface and they are required to satisfy boundary conditions at the surface. We shall discuss how the linear response functions can be calculated for finite media, incorporating the effects of surface excitations and bulk excitations together with their appropriate statistical weighting. This will be done for various different types of excitation and for various geometries.

Before giving a formal derivation of linear response theory in the next section, it is helpful to consider a simple mathematical example which will illustrate some of the basic concepts. We examine the case of a damped

harmonic oscillator in one dimension, where the displacement  $U$  describing the motion of a mass  $m$  fluctuates, having a natural resonance frequency  $\omega_0$ . Also let  $f(t)$  be a fictitious force which acts on the system in such a way that the interaction Hamiltonian has the simple form  $H_I = -Uf(t)$ . The driven equation of motion for the oscillator is therefore

$$m \left( \frac{d^2 U}{dt^2} + \Gamma \frac{dU}{dt} + \omega_0^2 U \right) = f(t), \quad (1.1)$$

where  $\Gamma$  is a positive constant which describes the damping. We may introduce Fourier transforms of the force and the particle displacement by

$$f(\omega) = \int_{-\infty}^{\infty} f(t) \exp(i\omega t) dt \quad (1.2a)$$

$$U(\omega) = \int_{-\infty}^{\infty} U(t) \exp(i\omega t) dt. \quad (1.2b)$$

The value  $\bar{U}$  of the displacement (averaged over an ensemble of oscillators with random phases) is different from zero owing to the action of the driving force  $f$ , and we may define a response function  $\chi(\omega)$  by

$$\chi(\omega) = \bar{U}(\omega)/f(\omega). \quad (1.3)$$

Using eqs. (1.1) and (1.2) it is easily shown that

$$\chi(\omega) = \frac{1}{m(\omega_0^2 - \omega^2 - i\Gamma\omega)}. \quad (1.4)$$

This complex quantity exhibits a resonant behavior at values of  $\omega$  equal to  $\pm \omega_0$ . It satisfies the symmetry property (see Landau and Lifshitz 1969) that

$$\chi(-\omega) = \chi^*(\omega), \quad (1.5)$$

where the asterisk denotes complex conjugation. This relationship implies that the real and imaginary parts of  $\chi(\omega)$  are respectively symmetric and antisymmetric functions of  $\omega$ .

An important property of the response function  $\chi(\omega)$  is that it is closely related to the absorption (or dissipation) of energy from the fictitious force  $f(t)$  [see Landau and Lifshitz (1969) for a detailed discussion]. We can illustrate this property by considering the damped harmonic oscillator with a periodic driving term  $f(t) = f_0 \cos \omega t$ . In this case it follows from previous definitions that

$$\bar{U}(t) = \frac{1}{2} f_0 [\chi(\omega) e^{-i\omega t} + \chi^*(\omega) e^{i\omega t}]. \quad (1.6)$$

From the form of the Hamiltonian  $H_I$  describing the interaction of the force

$f(t)$  with the system we calculate the average dissipation  $W$  per unit time as

$$W = -\bar{U}(t) \frac{df(t)}{dt} \\ = \frac{1}{4} i \omega f_0^2 [\chi^*(\omega) e^{2i\omega t} + \chi^*(\omega) + \chi(\omega) - \chi(\omega) e^{-2i\omega t}]. \quad (1.7)$$

When this is averaged over the period  $2\pi/\omega$  the result can be expressed as

$$W = \frac{1}{2} f_0^2 \omega \operatorname{Im} \chi(\omega). \quad (1.8)$$

On physical grounds we must have  $W \geq 0$ , and the above result therefore implies the stability condition that  $\omega \operatorname{Im} \chi(\omega) \geq 0$ . It can easily be checked that the response function  $\chi(\omega)$  of eq. (1.4) fulfils this requirement for any real frequency  $\omega$ .

The Fourier components  $\langle |U|^2 \rangle_\omega$  of the mean square displacement provide the power spectrum of fluctuations for the damped harmonic oscillator. The quantity  $\langle |U|^2 \rangle_\omega$  can be related to the dissipative properties of the system and hence to the imaginary part of  $\chi(\omega)$ . In the high-temperature "classical" limit of  $k_B T \gg \hbar \omega$  the connection is provided by

$$\langle |U|^2 \rangle_\omega = (k_B T / \pi \omega) \operatorname{Im} \chi(\omega), \quad (k_B T \gg \hbar \omega), \quad (1.9)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature. This is the classical form of the so-called fluctuation-dissipation theorem, or generalized Nyquist theorem. Its derivation has been discussed by many authors [see, for example, Callen and Welton (1951), Landau and Lifshitz (1969), MacDonald (1962), Kubo (1966), and references therein]. The more general quantum mechanical form of the fluctuation-dissipation theorem is similar to eq. (1.9), but with  $(k_B T / \pi \omega)$  replaced by another thermal factor as we shall discuss in section 2. For our example of the damped harmonic oscillator it follows from eqs. (1.4) and (1.9) that

$$\langle |U|^2 \rangle_\omega = \left( \frac{k_B T}{\pi m} \right) \frac{\Gamma}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2}. \quad (1.10)$$

For a lightly damped system (for which  $\Gamma \ll \omega_0$ ) the right-hand side of eq. (1.10) is effectively nonzero only for  $\omega$  close to  $\omega_0$  or  $-\omega_0$ , and this enables us to approximate by writing the result in a Lorentzian-like form as

$$\langle |U|^2 \rangle_\omega \approx \left( \frac{k_B T}{2\pi m \omega_0^2} \right) \frac{(\Gamma/2)}{(\omega_0 - |\omega|)^2 + (\Gamma/2)^2}. \quad (1.11)$$

The mean square value  $\langle |U|^2 \rangle$  of the fluctuating displacement is obtained from

$$\langle |U|^2 \rangle = \int_{-\infty}^{\infty} \langle |U|^2 \rangle_\omega d\omega. \quad (1.12)$$

When eq. (1.11) is substituted into eq. (1.12), and the integration over  $\omega$  is performed, we find that  $\langle |U|^2 \rangle \approx k_B T / m \omega_0^2$ , which is just the result expected according to the principle of equipartition of energy.

A physical situation in which the response function is well approximated by the damped harmonic oscillator result of eq. (1.4) is the description of long-wavelength optical lattice vibrations in a diatomic crystal. The variable  $U$  would denote the relative ionic displacement for a particular polarization,  $m$  would be an appropriately defined reduced ionic mass, and  $\omega_0$  would denote the frequency of the vibrations (independent of wavevector  $\mathbf{Q}$  in the long-wavelength limit).

In general, however, the response functions will depend on position labels (or alternatively on wavevector labels). For example, we could consider applying a fictitious force (or stimulus) to the system at a point with position vector  $\mathbf{x}'$  and measuring the response at some other point  $\mathbf{x}$ . The appropriately defined response function would then depend on  $\mathbf{x}$  and  $\mathbf{x}'$ , as well as the frequency  $\omega$ . For an effectively infinite system possessing translational invariance the dependence on  $\mathbf{x}$  and  $\mathbf{x}'$  appears only through the combination  $(\mathbf{x} - \mathbf{x}')$ . This enables a simple wavevector Fourier transform to be defined for the response function, so that the Fourier components depend on a single wavevector label  $\mathbf{Q}$ . On the other hand, this will not be the case for problems involving surfaces and interfaces. Owing to loss of translational symmetry perpendicular to any surface, the spatial response functions will depend on position labels  $\mathbf{x}$  and  $\mathbf{x}'$  individually, and a double Fourier transform to a wavevector representation is needed involving two labels  $\mathbf{Q}$  and  $\mathbf{Q}'$ .

The outline of this chapter is as follows. In section 2 we summarize linear response theory in a general form appropriate to systems either with or without translational symmetry. We establish the correspondence between linear response functions and the commutator Green's functions of quantum mechanics (see Zubarev 1960). The fluctuation-dissipation theorem is discussed, providing a simple connection between correlation functions and their corresponding response functions (or Green's functions). In particular we emphasize the usefulness of the linear response approach for investigating surface problems, and we illustrate the procedure for this in section 2 by means of a simple example. For the most part we shall consider only plane surfaces, and we restrict attention to simple geometries. These include the case of a semi-infinite medium (where only one surface need be considered), and the parallel-sided slab or film of finite thickness (where there are two surfaces). In sections 3 to 6 the general linear response theory is applied to various types of surface excitations, including phonons, magnons, magneto-static modes, and polaritons. Many of these topics will be considered in greater detail in subsequent chapters of this book. In section 7 we give a brief account of how surface response functions can be used to calculate

physical quantities, e.g. light scattering from absorptive media, thermodynamic properties, Kapitza resistance, etc. Section 8 contains a brief discussion of some extensions of the method, including piezoelectric and magneto-elastic media, spatial dispersion and surface roughness. The general conclusions are given in section 9.

Other general techniques for evaluating Green's functions, such as the microscopic approaches based on Green's function equations-of-motion or diagrammatic perturbation theory (see Zubarev 1960, Abrikosov et al. 1963), can of course also be applied to surface problems. However, they lack the direct physical appeal of linear response theory, which has the added advantage of being particularly convenient for performing calculations macroscopically (i.e. using a continuum approach for the solid or fluid). The macroscopic approach is a convenient simplification when dealing with long-wavelength excitations (where the wavelength is large compared with the interatomic distances), since the calculation of the response function (Green's function) involves solving a differential equation rather than the harder task of solving a set of *inhomogeneous* finite difference equations. There are in fact relatively few microscopic calculations of the Green's functions for surface problems, but as examples we mention the work of Maradudin and Melngailis (1964) for phonons and Cottam (1976a, 1978) for magnons in semi-infinite media. Another approach which has been employed in investigating surface excitations is the Green's function matching method of Garcia-Moliner and co-workers (see Garcia-Moliner 1977, Garcia-Moliner and Flores 1979).

## 2. General Linear Response Theory

In this section we describe some of the formal aspects of linear response theory. Some useful general references are Landau and Lifshitz (1969), Kubo (1966), Forster (1975) and Stinchcombe (1978). We shall here be concerned with developing the formalism in a way that is appropriate for application to surface problems. Subsection 2.1 deals with the definitions of response functions and Green's functions and the relationship between them, while subsection 2.2 is concerned with the fluctuation-dissipation theorem and the evaluation of correlation functions. The general techniques are illustrated in subsection 2.3 where we give a specific example of calculating a response function for a semi-infinite medium. Some further general properties, including symmetry relations, are then discussed in subsection 2.4.

### 2.1. Response Functions and Green's Functions

Let  $f(t)$  denote a fictitious field (or generalized "force") which couples linearly with a system variable represented by the operator  $U$  so that the



interaction Hamiltonian  $H_1$  is

$$H_1 = -Uf(t). \quad (2.1)$$

For example, if  $U$  represents a magnetic dipole moment then the corresponding  $f(t)$  would be a magnetic field. We suppose that at time  $t = -\infty$  the system is in equilibrium, described by the Hamiltonian  $H_0$  and the corresponding density matrix  $\rho_0 = e^{-\beta H_0} / \text{Tr}(e^{-\beta H_0})$ , where  $\beta = 1/k_B T$ . The perturbation  $H_1$  is then increased adiabatically from zero, so that at a later time  $t$  the density matrix is changed to

$$\rho = \rho_0 + \rho_1. \quad (2.2)$$

The equation of motion for the density matrix is (taking units such that  $\hbar = 1$ )

$$i d\rho/dt = [H_0 + H_1, \rho_0 + \rho_1]. \quad (2.3)$$

Hence retaining only terms which are linear in the perturbing field  $f(t)$  we obtain

$$i d\rho_1/dt = [H_0, \rho_1] - [U, \rho_0]f(t), \quad (2.4)$$

where we have used the result that  $H_0$  and  $\rho_0$  commute. Eq. (2.4) has the formal solution

$$\rho_1 = i \int_{-\infty}^t \exp[iH_0(t' - t)] [U, \rho_0] f(t') \exp[-iH_0(t' - t)] dt'. \quad (2.5)$$

This result for  $\rho_1$ , correct to first order in  $f$ , enables us to calculate the response of the system to the applied perturbation. This response can be expressed in terms of the change  $\bar{V}(t)$  that it produces in the mean value of any system variable denoted by the operator  $V$ . This is given by

$$\bar{V}(t) = \text{Tr}(\rho_1 V). \quad (2.6)$$

On substituting eq. (2.5) into eq. (2.6) and using the cyclic invariance property of operators within the trace, we may express the linear response as

$$\bar{V}(t) = i \int_{-\infty}^t \langle [V(t), U(t')] \rangle f(t') dt'. \quad (2.7)$$

Here  $\langle \dots \rangle = \text{Tr}(\rho_0 \dots)$  denotes a thermal average with respect to the unperturbed system, and

$$V(t) = e^{iH_0 t} V e^{-iH_0 t} \quad (2.8)$$

is the operator  $V$  in the Heisenberg picture, with a similar definition for  $U(t')$ . If we now define a linear response function  $\chi(t - t')$  (or generalized