

# Lectures on Theoretical Physics

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## Linear Response Theory

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The theory of linear response to perturbations of the equilibrium state, or linear response theory, is the subject of this series of lectures.

Ordinary matter, if left alone, will sooner or later attain an equilibrium state. This equilibrium state depends on the temperature of the environment and on external parameters. External parameters may be the region of space within which a certain number of particles are confined, mechanical stress, or the strength of an external electric or magnetic field.

If temperature or the external parameters change slowly enough, the system can attain the new equilibrium state practically instantaneously, and we speak of a reversible process. On the other hand, if the external parameters vary so rapidly that the system has no chance to adapt, it remains away from equilibrium, and we speak of irreversibility.

The most important application is optics. There is a medium which is exposed to an electromagnetic wave. The electric field changes so rapidly that matter within a region of micrometer dimensions cannot react instantaneously, it responds with retardation. We shall work out the retarded response in linear approximation.

There are quite a few general and important results which hold irrespective of a particular Hamiltonian, such as the Kramers-Kronig relations, the fluctuation-dissipation theorem, the second law of thermodynamics, and Onsager's relation.

We discuss various electro- and magneto-optic effects, such as the Pockels effect, the Faraday effect, the Kerr effect, and the Cotton-Mouton effect.

We also treat spatial dispersion, or optical activity and indicate how the theory is to be developed further in order to handle the non-linear response as well.

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## 1 Maxwell equations

In this series of lectures we will study the interaction of a rapidly oscillating electromagnetic field with matter. Therefore, a recollection of basic electrodynamics seems to be appropriate.

### 1.1 The electromagnetic field

The electromagnetic fields  $\mathbf{E} = \mathbf{E}(t, \mathbf{x})$  and  $\mathbf{B} = \mathbf{B}(t, \mathbf{x})$  are defined by their action on charged particles. The trajectory  $t \rightarrow \mathbf{x}(t)$  of a particle with charge  $q$  is a solution of

$$\dot{\mathbf{p}} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) , \quad (1.1)$$

where  $\mathbf{v} = \dot{\mathbf{x}}$  and  $\mathbf{p} = m\mathbf{v}/\sqrt{1 - \mathbf{v}^2/c^2}$ . The electromagnetic field is to be evaluated at the current particle location  $t, \mathbf{x}(t)$ .

The electromagnetic fields act on charged particles, as described by the Lorentz formula (1.1), and charged particles generate the electromagnetic field.  $dQ = dV \rho(t, \mathbf{x})$  is the amount of electric charge in a small volume element  $dV$  at  $\mathbf{x}$  at time  $t$ . Likewise,  $dI = d\mathbf{A} \cdot \mathbf{j}(t, \mathbf{x})$  is the charge current passing the small area element  $d\mathbf{A}$  from the back to the front side.

Maxwell's equations read

$$\epsilon_0 \nabla \cdot \mathbf{E} = \rho \quad \text{and} \quad \frac{1}{\mu_0} \nabla \times \mathbf{B} - \epsilon_0 \dot{\mathbf{E}} = \mathbf{j} \quad (1.2)$$

as well as

$$\nabla \cdot \mathbf{B} = 0 \quad \text{and} \quad \nabla \times \mathbf{E} + \dot{\mathbf{B}} = 0 . \quad (1.3)$$

The first group of four equations describe the effect of electric charge and current, the second group of likewise four equations say that there is no magnetic charge (magnetic monopoles).

It is a consequence of Maxwell's equations that charge is conserved,

$$\dot{\rho} + \nabla \cdot \mathbf{j} = 0 . \quad (1.4)$$

### 1.2 Potentials

Stationary fields decouple.

$$\epsilon_0 \nabla \cdot \mathbf{E} = \rho \quad \text{and} \quad \nabla \times \mathbf{E} = 0 \quad (1.5)$$

describe the electrostatic field,

$$\frac{1}{\mu_0} \nabla \times \mathbf{B} = \mathbf{j} \quad \text{and} \quad \nabla \cdot \mathbf{B} = 0 \quad (1.6)$$

the magnetostatic field.

The electrostatic field may be derived from a scalar potential,

$$\mathbf{E} = -\nabla\phi \quad (1.7)$$

which obeys Poisson's equation

$$-\epsilon_0\Delta\phi = \rho \quad (1.8)$$

The magnetostatic field can be expressed by

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (1.9)$$

in terms of a vector potential  $\mathbf{A}$ . Adding the gradient of an arbitrary scalar field  $\Lambda$ ,  $\mathbf{A}' = \mathbf{A} + \nabla\Lambda$ , does not change the induction field  $\mathbf{B}$ . This ambiguity allows to subject the vector potential to a gauge, e.g. the Coulomb gauge  $\nabla \cdot \mathbf{A} = 0$ . The three components of the vector potential the obey a Poisson equation each,

$$-\frac{1}{\mu_0}\Delta\mathbf{A} = \mathbf{j} \quad (1.10)$$

The full set of Maxwell equations are solved by

$$\mathbf{E} = -\nabla\phi - \dot{\mathbf{A}} \quad \text{and} \quad \mathbf{B} = \nabla \times \mathbf{A} \quad (1.11)$$

If we now impose the Lorentz gauge

$$\epsilon_0\dot{\phi} + \frac{1}{\mu_0}\nabla \cdot \mathbf{A} = 0 \quad (1.12)$$

the following equations result:

$$\epsilon_0\Box\phi = \rho \quad \text{and} \quad \frac{1}{\mu_0}\Box\mathbf{A} = \mathbf{j} \quad (1.13)$$

The box, or wave operator is  $\partial_0^2 - \Delta$  where  $\partial_0$  is the partial derivative with respect to time, divided by  $c$  which is defined as  $c = 1/\sqrt{\epsilon_0\mu_0}$ .

### 1.3 Field energy

The potential of a point charge  $q$  resting at  $\mathbf{y}$  is the Coulomb potential

$$\phi_C(\mathbf{x}) = \frac{q}{4\pi\epsilon_0} \frac{1}{|\mathbf{x} - \mathbf{y}|} \quad (1.14)$$

If charges  $q_1, q_2, \dots$  are brought from infinity to their locations at  $\mathbf{x}_1, \mathbf{x}_2, \dots$  the following work has to be done:

$$W = \sum_{b>a} \frac{1}{4\pi\epsilon_0} \frac{q_b q_a}{|\mathbf{x}_b - \mathbf{x}_a|} \quad (1.15)$$

For a smooth charge distribution  $\rho$  this expression may be rewritten into

$$W = \frac{1}{8\pi\epsilon_0} \int \frac{d^3x'' d^3x' \rho(\mathbf{x}'') \rho(\mathbf{x}')}{|\mathbf{x}'' - \mathbf{x}'|} = \frac{1}{2} \int d^3x \rho(\mathbf{x}) \phi(\mathbf{x}) . \quad (1.16)$$

By partial integration we obtain

$$W = \int d^3x \frac{\epsilon_0 \mathbf{E}^2}{2} . \quad (1.17)$$

We interpret  $\epsilon_0 \mathbf{E}^2/2$  as the energy density of the electric field.

Using Maxwell's equation we may prove the following balance equation:

$$\dot{\eta} + \nabla \cdot \mathbf{S} = \eta^* \quad (1.18)$$

where

$$\eta = \frac{\epsilon_0 \mathbf{E}^2}{2} + \frac{\mathbf{B}^2}{2\mu_0} , \quad \mathbf{S} = \frac{1}{\mu_0} \mathbf{E} \times \mathbf{B} \quad \text{and} \quad \eta^* = -\mathbf{j} \cdot \mathbf{E} . \quad (1.19)$$

As explained before,  $\epsilon_0 \mathbf{E}^2/2$  is the energy density of the electric field. The energy density of the magnetic field is  $\mathbf{B}^2/2\mu_0$ . The energy current density  $\mathbf{S} = (\mathbf{E} \times \mathbf{B})/\mu_0$  is also called Poynting's vector.

$\eta^* = -\mathbf{j} \cdot \mathbf{E}$  describes the production of field energy per unit time per unit volume. Field energy is created if charge runs counter to the electric field (Bremsstrahlung). Field energy vanishes if charges run with the direction of the electric field (Ohm's law, Joule's heat).

#### 1.4 Polarization and magnetization

$Q = \int d^3x \rho(\mathbf{x})$  is the charge of system. By  $\mathbf{p} = \int d^3x \mathbf{x} \rho(\mathbf{x})$  we denote its electric dipole moment. The dipole moment does not depend on the choice of the coordinate system origin if its charge vanishes.

Denote by  $\mathbf{P}$  the density of a probe's dipole moments, its polarization. For ordinary matter, which is locally neutral, this is a well defined quantity. One can show that  $-\nabla \cdot \mathbf{P}$  is the charge density causing the polarization and that  $\dot{\mathbf{P}}$  contributes to the current density.

We likewise define magnetic dipole moments  $\mathbf{m}$  and their density  $\mathbf{M}$ , the magnetization.  $\nabla \times \mathbf{M}$  also contributes to the current density. The charge and current density should therefore be split into

$$\rho = -\nabla \cdot \mathbf{P} + \rho^f \quad \text{and} \quad \mathbf{j} = \dot{\mathbf{P}} + \nabla \times \mathbf{M} + \mathbf{j}^f . \quad (1.20)$$

The remainders  $\rho^f$  and  $\mathbf{j}^f$  are the charge and current density of free, or mobile charges, as opposed to bound charges.

We introduce auxiliary fields  $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$  (dielectric displacement) and  $\mathbf{H} = \mathbf{B}/\mu_0 - \mathbf{M}$  (magnetic field strength). They obey the following equations:

$$\nabla \cdot \mathbf{D} = \rho^f \quad \text{and} \quad \nabla \times \mathbf{H} - \dot{\mathbf{D}} = \mathbf{j}^f . \quad (1.21)$$

$$\nabla \cdot \mathbf{B} = 0 \quad \text{and} \quad \nabla \times \mathbf{E} + \dot{\mathbf{B}} = 0 \quad (1.22)$$

remain unchanged.

## 2 A simple model

For warming up, we develop a very simple model of the dielectric susceptibility. Consider an atom which is exposed to an oscillating electric field  $E = E(t)$  along the  $z$ -direction. A particular electron of this atom will be forced to oscillate.

### 2.1 Equation of motion

We assume that the electron's equilibrium position is  $z = 0$ . There is an equilibrium restoring counter force which, for small deviations, will be proportional to  $z$ . We also allow for friction which we assume to be proportional to the electrons velocity  $\dot{z}$ . Therefore, the following equation of motion has to be solved:

$$\ddot{z} + 2\eta\dot{z} + \Omega_0^2 z = a(t) \quad \text{where} \quad a(t) = -\frac{e}{m}E(t) . \quad (2.1)$$

$m$  and  $-e$  are the electron's mass and charge,  $m\Omega_0^2$  is the spring constant of the linear oscillator,  $2m\eta$  the friction coefficient.

### 2.2 Green's function

Because there is a linear relationship between position  $z$  and acceleration  $a$  we should write

$$z(t) = \int ds \Gamma(t, s) a(s) , \quad (2.2)$$

where  $\Gamma$  is a Green function.

Because the coefficients of the differential equation (2.1) do not depend on time  $t$  one has  $\Gamma(t, s) = \Gamma(t - s)$ . This implies

$$z(t) = \int ds \Gamma(t - s) a(s) = \int d\tau \Gamma(\tau) a(t - \tau) . \quad (2.3)$$

$\tau$  is the time difference between cause (accelerating force, or  $a$ ) and effect (deviation from equilibrium position,  $z$ ). Causes must be earlier than their effects, therefore

$$z(t) = \int_{-\infty}^t ds \Gamma(t - s) a(s) = \int_0^{\infty} d\tau \Gamma(\tau) a(t - \tau) . \quad (2.4)$$

$\tau$  is an age, it cannot be negative.

We differentiate (2.4) with respect to time,

$$\dot{z}(t) = \Gamma(0) a(t) + \int_{-\infty}^t ds \dot{\Gamma}(t - s) a(s) , \quad (2.5)$$

and likewise for  $\ddot{z}(t)$ .



Inserting these expressions into (2.1) results in

$$\ddot{\Gamma} + 2\eta\dot{\Gamma} + \Omega_0^2\Gamma = 0 \quad (2.6)$$

and

$$\Gamma(0) = 0 \quad \text{and} \quad \dot{\Gamma}(0) = 1 \quad . \quad (2.7)$$

This differential equation with constant coefficients is solved by  $\Gamma \propto e^{\Lambda t}$  which implies  $\Lambda^2 + 2\eta\Lambda + \Omega_0^2 = 0$ , i.e.  $\Lambda = -\eta \pm i\Omega$  where

$$\Omega = \sqrt{\Omega_0^2 - \eta^2} \quad . \quad (2.8)$$

We assume weak damping,  $\eta/\Omega_0 < 1$ . The two fundamental solutions are to be superimposed such that the initial condition (2.7) are satisfied. We obtain

$$\Gamma(\tau) = \frac{1}{\Omega} e^{-\eta\tau} \sin \Omega\tau \quad . \quad (2.9)$$

The original equation of motion has thus been solved for an arbitrary oscillating electric field strength  $E = E(t)$ .

### 2.3 Susceptibility

$p = -ez$  is the dipole moment of the electron under consideration. If there are  $N$  of them per unit volume, the polarization is  $P = Np$ . We just have obtained the result

$$P(t) = \frac{Ne^2}{m} \int_0^\infty d\tau \Gamma(\tau) E(t - \tau) \quad . \quad (2.10)$$

Let us Fourier decompose the electric field strength:

$$E(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} \hat{E}(\omega) \quad . \quad (2.11)$$

We work out

$$P(t) = \epsilon_0 \int \frac{d\omega}{2\pi} e^{-i\omega t} \chi(\omega) \hat{E}(\omega) \quad (2.12)$$

where

$$\chi(\omega) = \frac{Ne^2}{m\epsilon_0} \int_0^\infty d\tau e^{i\omega\tau} \Gamma(\tau) = \frac{Ne^2}{m\epsilon_0} \frac{1}{(\Omega + \omega + i\eta)(\Omega - \omega - i\eta)} \quad . \quad (2.13)$$

The Fourier component  $\hat{P}(\omega)$ , which is declared in analogy to (2.11), is proportional to the Fourier component  $\hat{E}(\omega)$  at the same angular frequency  $\omega$ :

$$\hat{P}(\omega) = \epsilon_0 \chi(\omega) \hat{E}(\omega) \quad . \quad (2.14)$$

$\chi = \chi(\omega)$  is called the susceptibility of the material under study. It is a function of angular frequency. Note that we may rewrite (2.13) as

$$\chi(\omega) = \frac{Ne^2}{m\epsilon_0} \frac{1}{\Omega_0^2 - \omega^2 - 2i\eta\omega} . \quad (2.15)$$

(2.13) is an oversimplification because not all electrons have the same resonance frequency  $\Omega_0$  and the same damping constant  $\eta$ ; in fact, one must sum over such terms. However, (2.15) or a sum over such terms reflect the essential features quite well:

- The static value  $\chi(0)$  is always positive and real.
- $\chi(\omega) \rightarrow 0$  with  $\omega \rightarrow \infty$ .
- The imaginary part of the susceptibility is always non-negative.
- The imaginary part of the susceptibility is large close to a resonance  $\omega \approx \Omega_0$ .
- Dispersion is unavoidable, susceptibilities must be different for different angular frequencies.

### 3 Thermodynamic equilibrium

In this series of lectures we will study the interaction of a rapidly oscillating electromagnetic field with matter. Therefore, a recollection of basic statistical thermodynamics seems to be appropriate.

#### 3.1 Observables and states

We describe the system quantum-mechanically, i. e. by an appropriate Hilbert space  $\mathcal{H}$ . Observables  $M$ , or measurable quantities, are represented by self-adjoint linear operators mapping the Hilbert space into itself,  $M : \mathcal{H} \rightarrow \mathcal{H}$ . As is well known, the eigenvectors of self-adjoint operators form a complete system of normalized and mutually orthogonal vectors. The eigenspaces of an observable  $M$  describe the alternatives, the eigenvalues the measured values of these alternatives.

Pure states of the system are represented by wave functions, or vectors of  $\mathcal{H}$ . For a large system, the notion of a pure state is an oversimplification. In fact, there is a complete system of normalized and mutually orthogonal vectors  $\phi_1, \phi_2, \dots$  and a set of probabilities  $w_1, w_2, \dots$ . The  $w_j$  are the probabilities that the system will be found to be in the pure state  $\phi_j$ .

There is a unique linear operator  $W$  such that the  $\phi_j$  are its eigenvectors and the  $w_j$  its eigenvalues,

$$W\phi_j = w_j\phi_j \quad . \quad (3.1)$$

This probability operator<sup>1</sup>  $W$  describes the state of the system. It is characterized by

$$0 \leq W \leq 1 \quad \text{and} \quad \text{tr} W = 1 \quad . \quad (3.2)$$

Here 0 and 1 stand for the zero and the unity operator, and  $\text{tr}$  denotes the trace. (3.2) boils down to  $0 \leq w_j \leq 1$  and  $\sum w_j = 1$ .

The expectation value  $\langle M \rangle$  of the observable  $M$ , while the system is in state  $W$ , is given by

$$\langle M \rangle = \sum_j w_j (\phi_j, M\phi_j) = \text{tr} WM \quad . \quad (3.3)$$

#### 3.2 The first law of thermodynamics

The energy observable  $H$  (the Hamiltonian) is of particular interest because it governs the time development of the system. Its expectation value is conventionally denoted by  $U$ , the internal energy. It is a convention that thermodynamic systems are at rest, hence energy is internal energy.

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<sup>1</sup>also density matrix

The internal energy of a system may change because the state changes or because the Hamiltonian changes,

$$\delta U = \text{tr } \delta W H + \text{tr } W \delta H . \quad (3.4)$$

The first contribution  $\delta Q = \text{tr } \delta W H$  is heat, the second contribution  $\delta A = \text{tr } W \delta H$  is work<sup>2</sup>. The Hamiltonian usually depends on external parameters which may change. An external electric field is a typical example. The statement  $\delta U = \delta Q + \delta A$  is the first law of thermodynamics: energy may be transferred to a system as heat or as work.

### 3.3 Entropy

A mixed state  $W$  is a mixture of pure states. The pure states  $\phi_j$  are contained in the mixed state  $W$  with probabilities  $w_j$ . Two mixed states  $W_1$  and  $W_2$  may be further mixed to become  $W = \alpha_1 W_1 + \alpha_2 W_2$  where  $0 \leq \alpha_1, \alpha_2 \leq 1$  and  $\alpha_1 + \alpha_2 = 1$ . It is a simple exercise to show that  $0 \leq W \leq 1$  holds as well as  $\text{tr } W = 1$ .

We require a measure to answer the question: how much mixed is a state. This measure should vanish if  $W$  represents a pure state, and it should increase upon mixing. Here we just report the result of a lengthy discussion:

$$S(W) = k_B \sum_j w_j \ln \frac{1}{w_j} = -k_B \text{tr } W \ln W \quad (3.5)$$

is a measure of the degree of mixture.  $S(W)$  is the entropy of the mixed state  $W$ . The Boltzmann constant  $k_B$  shows up for purely historical reasons.

If all probabilities  $w_j$  equal zero, up to one, which must be unity, than the entropy vanishes. The entropy of a pure state vanishes. It can also be shown that

$$\alpha_1 S(W_1) + \alpha_2 S(W_2) \leq S(\alpha_1 W_1 + \alpha_2 W_2) \quad (3.6)$$

is true for states  $W_1, W_2$  and weights  $\alpha_1, \alpha_2$ . Mixing increases entropy.

### 3.4 The second law of thermodynamics

Assume a system which is well isolated from its environment. The internal energy within the system remains constant. Nevertheless, the environment will influence the time evolution of the system. The second law of thermodynamics states that the interactions between the system and its partially chaotic environment will increase the amount of chaos within the system which is measured by the entropy of its state. Put otherwise, the entropy of the system's state increases in the course of time.

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<sup>2</sup>German *Arbeit*. The symbol  $W$  (for work) is already in use (for the probability operator, or state)

It increases until it has reached a maximum. The state with maximal entropy does not change any more, it describes the equilibrium of the system with respect to its environment. Let us denote this equilibrium state by  $G$ . Denote by

$$\mathcal{S} = \{W : \mathcal{H} \rightarrow \mathcal{H} \mid 0 \leq W \leq 1, \text{tr } W = 1\} \quad (3.7)$$

the set of states. The equilibrium state, or Gibbs state, is characterized by

$$S(G) = \max_{W \in \mathcal{S}} S(W) \quad , \quad (3.8)$$

which amounts to

$$S(G + \delta W) = S(G) \quad \text{for} \quad \text{tr } \delta W = 0 \quad \text{and} \quad \text{tr } \delta W H = 0 \quad (3.9)$$

for small deviations  $\delta W$ .  $G + \delta W$  must be a state, and  $U = \text{tr}(G + \delta W)H$  should remain constant.

The solution of this problem reads

$$G = e^{(F - H)/k_B T} \quad , \quad (3.10)$$

where  $F$  and  $T$  are Lagrange multipliers.  $F$ , the free energy, is a number.  $H$  is the Hamiltonian of the system, and  $T$  the temperature of the Gibbs state.

The free energy is calculated according to

$$F = -k_B T \ln \text{tr } e^{-H/k_B T} \quad (3.11)$$

such that  $\text{tr } G = 1$  holds. The temperature  $T$  is determined by solving

$$U = \frac{\text{tr } H e^{-H/k_B T}}{\text{tr } e^{-H/k_B T}} \quad (3.12)$$

for  $T$ . One can show that the right hand side of (3.10) increases with the temperature  $T$  which guarantees a unique solution. Adding energy to a system, by heat or work, will make it warmer.

### 3.5 Irreversible processes

We denote the external parameters summarily by  $\lambda$ , i. e.  $H = H(\lambda)$ . The free energy depends on the temperature and on the external parameters,  $F = F(T, \lambda)$ . One can easily show that

$$dF = -SdT - \sum V_r d\lambda_r \quad (3.13)$$

holds true where

$$S = S(G) \quad (3.14)$$

is the entropy of the Gibbs state. The generalized forces  $V_r$  are given by

$$V_r = - \operatorname{tr} G \frac{\partial H(\lambda)}{\partial \lambda_r} . \quad (3.15)$$

We speak of a process if the temperature  $T = T_t$  of the system's environment and the external parameters  $\lambda_r = \lambda_{r,t}$  change in the course of time. The process is reversible provided the state  $W_t$  of the system is always very close to the corresponding equilibrium state,

$$W_t \simeq G(T_t, \lambda_t) . \quad (3.16)$$

If the external parameters change too rapidly, the system will remain away from equilibrium, and we speak of irreversible processes. With light, the typical spatial dimensions of material points are micrometers, and the corresponding period is  $3 \times 10^{14}$  s. This time is much too short for achieving equilibrium. The interaction of light with matter is an irreversible process. We will describe in the following sections how to cope with this problem.

## 4 Perturbing the equilibrium

In this section we will describe how the state of a system changes with time. We concentrate on small perturbations of the equilibrium state.

### 4.1 Time evolution

So far we have spoken of preparing a state  $W$  and immediately measuring an observable  $M$ . Let us now discuss the situation that we wait for a certain time  $t$  between preparing  $W$  and measuring  $M$ .

Let us first discuss the Heisenberg picture of time evolution. Waiting the time span  $t$  and then measuring  $M$  is a new observable  $M_t$ .  $M_t$  must be self-adjoint. Its eigenvalues, the possible outcomes of a measurement, are independent on the waiting time span  $t$ . Therefore,

$$M_t = U_{-t} M U_t \quad (4.1)$$

holds where  $U_t$  is a unitary operator.

Because of

$$U_{t_1+t_2} = U_{t_2} U_{t_1} \quad (4.2)$$

we conclude that  $U$  depends exponentially on  $t$ ,

$$U_t = e^{-\frac{i}{\hbar} t H} \quad (4.3)$$

where  $H$  is a self-adjoint operator, the Hamiltonian, or the energy. Note that (4.3) results in

$$\frac{d}{dt} M_t = \frac{i}{\hbar} [H, M_t] , \quad (4.4)$$

the Heisenberg equation of motion.  $[A, B] = AB - BA$  is the commutator of  $A$  with  $B$ .

Another aspect is the Schrödinger picture. Conceptually, preparing  $W$  and waiting a certain time  $t$  is preparing a state  $W_t$ . Because of

$$\text{tr} W M_t = \text{tr} W U_{-t} M U_t = \text{tr} U_t W U_{-t} M \quad (4.5)$$

we have to write

$$W_t = U_t W U_{-t} . \quad (4.6)$$

We have made use of  $\text{tr} AB = \text{tr} BA$ .

(4.6) results in the Schrödinger equation for mixed states, namely

$$\frac{d}{dt} W_t = \frac{i}{\hbar} [W_t, H] . \quad (4.7)$$

## 4.2 Interaction picture

Very often the Hamiltonian may be split into a manageable, time independent part  $H$  and a small perturbation  $V = V_t$  which may depend on time. Just think of  $H$  as the Hamiltonian of matter and  $V_t$  describing the perturbation by the electric field of a light wave.

It is then useful to work in the Heisenberg picture with respect to  $H$  only.

In the Schrödinger picture we have to solve

$$\frac{d}{dt}W_t = \frac{i}{\hbar} [W_t, H + V_t] . \quad (4.8)$$

With

$$A(t) = U_{-t}AU_t \quad (4.9)$$

where the time translation operator  $U_t$  is defined by (4.3) we arrive at

$$\frac{d}{dt}W_t(t) = U_{-t} \left\{ \frac{i}{\hbar} [H, W_t] + \frac{i}{\hbar} [W_t, H + V_t] \right\} U_t \quad (4.10)$$

or

$$\frac{d}{dt}W_t(t) = \frac{i}{\hbar} [W_t(t), V_t(t)] . \quad (4.11)$$

This equation of motion is driven by the perturbation only. If there were no  $V = V_t$ , then  $W_t(t)$  would be constant. It is to be expected that a small perturbation will cause the state  $W_t(t)$  to change only slowly.

## 4.3 Perturbing the Gibbs state

Assume that we perturb the Gibbs state:

$$W_t \rightarrow G = e^{(F - H)/k_B T} \quad \text{and} \quad V_t \rightarrow 0 \quad \text{for} \quad t \rightarrow -\infty . \quad (4.12)$$

Because the Gibbs state is stationary with respect to  $H$ , i. e.  $G(t) = G$ , we may also write

$$W_t(t) \rightarrow G \quad \text{for} \quad t \rightarrow -\infty . \quad (4.13)$$

By combining the initial condition (4.13) with (4.10) we arrive at the following integral equation:

$$W_t(t) = G + \int_{-\infty}^t ds \frac{i}{\hbar} [W_s(s), V_s(s)] . \quad (4.14)$$

This integral equation gives rise to a perturbation expansion with respect to  $V$ . In lowest order we have to set  $W_t(t) = G + \dots$ . In first order we arrive at

$$W_t(t) = G + \int_{-\infty}^t ds \frac{i}{\hbar} [G, V_s(s)] + \dots . \quad (4.15)$$

Inserting the first order expression (4.15) into (4.14) will result in the second order approximation, and so forth.



#### 4.4 Time dependent external parameter

We now specialize to

$$V_t = - \sum_r \lambda_r(t) V_r . \quad (4.16)$$

$\lambda_r = \lambda_r(t)$  is an external parameter,  $V_r$  the corresponding generalized force, an observable. We may rewrite the linear response (4.15) of the system to a perturbation of the equilibrium state into the following form:

$$W_t(t) = G - \int_{-\infty}^t ds \sum_r \lambda_r(s) \frac{i}{\hbar} [G, V_r(s)] + \dots , \quad (4.17)$$

or

$$W_t = G - \int_{-\infty}^t ds \sum_r \lambda_r(s) \frac{i}{\hbar} [G, V_r(s-t)] + \dots . \quad (4.18)$$

The expectation value of an observable  $M$  is

$$\text{tr } W_t M = \text{tr } G M + \int_0^\infty d\tau \sum_r \lambda_r(t-\tau) \Gamma(MV_r; \tau) + \dots \quad (4.19)$$

where

$$\Gamma(MV_r; \tau) = \text{tr } G \frac{i}{\hbar} [M(\tau), V_r] . \quad (4.20)$$

This is a remarkable result. The expectation value of an observable  $M$  is its equilibrium expectation value plus an additional contribution. The addition depends on past perturbations only. It is proportional to the external parameters  $\lambda_r$ . The Green function  $\Gamma = \Gamma(MV_r; \tau)$  depends on the age  $\tau$  of the perturbation and is linear in the perturbing generalized forces  $V_r$ . In fact, the commutator  $[M(t), V_r(s)]$  will vanish unless  $V_r(s)$  and  $M(t)$  affect each other. What is most important: the Green function is an expectation value of the unperturbed state  $G$ . Loosely speaking, the Gibbs state  $G$  knows already how it will react on perturbations.

## 5 Dielectric susceptibility

We now specialize to ordinary matter in an oscillating electric field. We may write

$$H = \sum_a \frac{\mathbf{p}_a^2}{2m_a} + \frac{1}{4\pi\epsilon_0} \sum_{b>a} \frac{q_b q_a}{|\mathbf{x}_b - \mathbf{x}_a|} \quad (5.1)$$

for the Hamiltonian of matter. Charged particles, nuclei and electrons, interact via Coulomb forces.  $a, b \dots$  label the particles,  $m_a$  and  $q_a$  are the respective masses and charges.  $\mathbf{x}_a$  and  $\mathbf{p}_a$  denote the particle positions and momenta, they are observables. This is no treatise on many particle physics, and (5.1) serves only to introduce notation. In particular, spin and relativistic effects are missing.

### 5.1 Polarization of matter

If there is an electromagnetic field, the interaction with matter can be classified by a multi-pole expansion. For our purpose, the electric dipole approximation is sufficient.

We define by

$$\mathbf{P}(x) = \sum_a q_a \mathbf{x}_a \delta^3(x - \mathbf{x}_a) \quad (5.2)$$

the density of dipole moments, or polarization as a field of observables. The interaction of the external electromagnetic field with matter is described in electric dipole approximation by

$$V_t = - \int d^3y \mathbf{E}(t, y) \cdot \mathbf{P}(y) \quad (5.3)$$

We assume a dielectric material, in contrast with a ferroelectric material. Without electric field there is no polarization,  $\text{tr } G\mathbf{P}(x) = 0$ . By inserting (5.3) into (4.19) and (4.20) we arrive at the following expression for the time-dependent polarization:

$$P_i(t, x) = \text{tr } W_t P_i(x) = \int_0^\infty d\tau \int d^3y \Gamma_{ij}(\tau, x, y) E_j(t - \tau, y) \quad (5.4)$$

Here and later we rely on Einstein's summation convention: a sum over the doubly occurring index  $j$  is silently understood.

The tensor of Green functions<sup>3</sup> is given by

$$\Gamma_{ij}(\tau, x, y) = \text{tr } G \frac{i}{\hbar} [P_i(\tau, x), P_j(0, y)] \quad (5.5)$$

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<sup>3</sup> $\Gamma_{ij}(\tau, x, y) = \Gamma(P_i(x)P_j(y); \tau)$  in the notation of section 4

Recall the definition of the polarization  $P_i(x)$  and its time translation

$$P_i(t, x) = U_{-t} P_i(x) U_t \quad \text{where} \quad U_t = e^{-\frac{i}{\hbar} t H} . \quad (5.6)$$

Also recall the definition of the equilibrium, or Gibbs state

$$G = e^{(F - H)/k_B T} . \quad (5.7)$$

$H$  in (5.6) and (5.7) is the Hamiltonian (5.1) of unperturbed matter.

We assume that the Gibbs state is not only invariant with respect to time translations, but also with respect to spatial translations. One may then write

$$\Gamma_{ij}(\tau, \xi) = \text{tr} G \frac{i}{\hbar} [P_i(\tau, \xi), P_j(0, 0)] \quad (5.8)$$

instead of (5.5) and

$$P_i(t, x) = \text{tr} W_t P_i(x) = \int_0^\infty d\tau \int d^3\xi \Gamma_{ij}(\tau, \xi) E_j(t - \tau, x - \xi) \quad (5.9)$$

instead of (5.4).

## 5.2 Dielectric susceptibility

Let us Fourier decompose the external electric field:

$$E_i(t, x) = \int \frac{d\omega}{2\pi} e^{-i\omega t} \int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{q} \cdot \mathbf{x}} \hat{E}_i(\omega, q) . \quad (5.10)$$

We may likewise decompose the polarisation<sup>4</sup>  $P_i(t, x)$ .

The well-know convolution theorem of Fourier theory allows to write

$$\hat{P}_i(\omega, q) = \epsilon_0 \chi_{ij}(\omega, q) \hat{E}_j(\omega, q) \quad (5.11)$$

where

$$\chi_{ij}(\omega, q) = \frac{1}{\epsilon_0} \int_0^\infty d\tau e^{i\omega\tau} \int d^3\xi e^{-i\mathbf{q} \cdot \boldsymbol{\xi}} \Gamma_{ij}(\tau, \xi) \quad (5.12)$$

is the tensor of dielectric susceptibility. It is a simple exercise to verify that the susceptibilities are dimensionless. If we could solve all equations which we may write down, the susceptibility of any material can be calculated. It depends on frequency, on the wave vector, on temperature, and on all other parameters which characterize the equilibrium state.

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<sup>4</sup>We use the same word for the observable  $P_i = P_i(x)$  and its expectation value in the time dependent state  $W_t$ , i.e.  $P_i(t, x) = \text{tr} W_t P_i(x)$ .

### 5.3 Susceptibility proper and optical activity

Since the velocity of sound, which sets the time to distance scale in solids, is so much smaller than the velocity of light, the susceptibility varies only weakly with the wave number. We may expand

$$\chi_{ij}(\omega, q) = \chi_{ij}(\omega) + \chi_{ijk}(\omega) q_k + \dots \quad (5.13)$$

In most optical applications only  $\chi_{ij}(\omega)$  is required. The frequency dependent tensor  $\chi_{ij}(\omega)$  is likewise called the susceptibility of the material in question. The next term describes optical activity. Higher order expansion coefficients are seldom encountered. Optical activity is deferred to a later section. In the following we are concerned entirely with the ordinary frequency dependent susceptibility tensor  $\chi_{ij}(\omega)$ ,

$$\chi_{ij}(\omega) = \frac{1}{\epsilon_0} \int_0^\infty d\tau e^{i\omega\tau} \int d^3\xi \operatorname{tr} G \frac{i}{\hbar} [P_i(\tau, \xi), P_j(0, 0)] \quad (5.14)$$

## 6 Dispersion relations

We will now exploit the fact that the response to a perturbation is retarded. The generalized susceptibility is given by

$$\chi(AB; \omega) = \int_0^{\infty} d\tau e^{i\omega\tau} \Gamma(AB; \tau) , \quad (6.1)$$

where the response function is

$$\Gamma(AB; \tau) = \text{tr} G \frac{i}{\hbar} [A(\tau), B(0)] . \quad (6.2)$$

It weighs the impact of a perturbation caused by  $B$  on  $A$  after a delay  $\tau$ . See appendix A for a summary on causal functions.

### 6.1 Retarded Green function

In fact, the generalized susceptibility is the Fourier transform of a product,

$$\chi(AB; \omega) = \int d\tau e^{i\omega\tau} \theta(\tau) \Gamma(AB; \tau) , \quad (6.3)$$

where  $\theta = \theta(x)$  is the Heaviside<sup>5</sup> jump function, a distribution.

The Fourier transform of a product is the convolution of the respective Fourier transforms,

$$\chi(AB; \omega) = \int \frac{du}{2\pi} \hat{\theta}(\omega - u) \hat{\Gamma}(AB; u) . \quad (6.4)$$

The Fourier transform of the Heaviside function is

$$\hat{\theta}(\omega) = \int_0^{\infty} dt e^{(i\omega - \epsilon)t} = \frac{i}{\omega + i\epsilon} . \quad (6.5)$$

$\epsilon$  is a positive, yet arbitrarily small number. Therefore,

$$\chi(AB; \omega) = \frac{1}{2\pi i} \int \frac{du}{u - \omega - i\epsilon} \hat{\Gamma}(AB; u) . \quad (6.6)$$

(6.6) says that the pole at  $u = \omega$  is to be avoided by running in the lower complex plane.

Now, the Gibbs state is stationary, therefore

$$\langle \frac{i}{\hbar} [A(\tau), B(0)] \rangle = \langle \frac{i}{\hbar} [A(0), B(-\tau)] \rangle \quad (6.7)$$

holds true which implies

$$\Gamma(AB; \tau) = \Gamma(BA; -\tau) \quad (6.8)$$

---

<sup>5</sup> $\theta(x) = 0$  for  $x < 0$  and  $\theta(x) = 1$  for  $x > 0$

or

$$\hat{\Gamma}(AB; \omega) = -\hat{\Gamma}(BA; -\omega) = -\hat{\Gamma}(BA; \omega)^* . \quad (6.9)$$

The last conclusion relies on the fact that response functions  $\Gamma(AB; \tau)$  are real. With this information we may work out

$$\chi(BA; \omega)^* = \frac{1}{2\pi i} \int \frac{du}{u - \omega + i\epsilon} \Gamma(AB; u) . \quad (6.10)$$

Note the similarity with (6.6). The only difference is how to evade the singularity  $u = \omega$ . The difference of (6.6) and (6.10) is a ring integral around the singularity, it results in

$$\chi(AB; \omega) - \chi(BA; \omega)^* = \hat{\Gamma}(AB; \omega) . \quad (6.11)$$

We define the refractive part of the susceptibility by

$$\chi'(AB; \omega) = \frac{\chi(AB; \omega) + \chi(BA; \omega)^*}{2} \quad (6.12)$$

and the absorptive part by

$$\chi''(AB; \omega) = \frac{\chi(AB; \omega) - \chi(BA; \omega)^*}{2i} . \quad (6.13)$$

Both are Hermitian in the sense that interchanging  $A$  and  $B$  as well as complex conjugating it leave the expressions unchanged.

Inserting  $\hat{\Gamma}(AB; \omega) = 2i\chi''(AB; \omega)$  into the sum of (6.6) and (6.10) we arrive at

$$\chi'(AB; \omega) = \frac{1}{\pi} \text{Pr} \int \frac{du}{u - \omega} \chi''(AB; u) . \quad (6.14)$$

The principal value of the integral is the mean of avoiding the singularity via the upper and the lower complex  $u$ -plane. It may also be defined by

$$\text{Pr} \int \frac{du}{u - \omega} f(u) = \left( \int_{-\infty}^{\omega - \epsilon} + \int_{\omega + \epsilon}^{\infty} \right) \frac{du}{u - \omega} f(u) . \quad (6.15)$$

(6.15) is the prototype of a dispersion relation. In the following subsection we will specialize to optics thereby justifying the terminology: refractive, absorptive, dispersion.

## 6.2 Kramers-Kronig relations

Recall the definition of the dielectric susceptibility tensor

$$\chi_{ij}(\omega) = \frac{1}{\epsilon_0} \int_0^\infty d\tau e^{-i\omega\tau} \int d^3\xi \operatorname{tr} G \frac{i}{\hbar} [P_i(\tau, \xi), P_j(0, 0)] . \quad (6.16)$$

It fits into the general scheme,

$$\chi_{ij}(\omega) = \int d^3\xi \chi(P_i(\xi)P_j(0); \tau) . \quad (6.17)$$

Response functions  $\Gamma(AB; \tau)$  and their susceptibilities  $\chi(AB; \omega)$  are linear in both arguments,  $A$  and  $B$ , and the same can be said of the dispersion relation (6.16). It can be summed over  $A$  and remains true.

With

$$\chi'_{ij}(\omega) = \frac{\chi_{ij}(\omega) + \chi_{ji}(\omega)^*}{2} \quad (6.18)$$

and

$$\chi''_{ij}(\omega) = \frac{\chi_{ij}(\omega) - \chi_{ji}(\omega)^*}{2i} \quad (6.19)$$

we may write

$$\chi'_{ij}(\omega) = \frac{1}{\pi} \operatorname{Pr} \int \frac{du}{u - \omega} \chi''_{ij}(u) . \quad (6.20)$$

This particular form of a dispersion relation is known as the Kramers-Kronig relation. It first of all explains why refraction depends on frequency. A beam of natural light consists of many colors, and a glass prism will lead to dispersion. The Kramers-Kronig relation also tells that there is no refraction without absorption, although at different frequencies. It remains to show that the absorptive part  $\chi''_{ij}(\omega)$  is a non-negative Hermitian tensor.

## 6.3 Refraction and absorption

We discuss Maxwell's equations for purely periodic fields in absence of charges and currents:

$$\nabla \times \mathbf{H} = -i\omega\epsilon_0\epsilon\mathbf{E} \quad \text{and} \quad \nabla \times \mathbf{E} = i\omega\mu_0\mathbf{H} . \quad (6.21)$$

The remaining divergence equations are automatically fulfilled.

The permittivity tensor  $\epsilon$  of (6.21) is

$$\epsilon_{ij}(\omega) = \delta_{ij} + \chi_{ij}(\omega) . \quad (6.22)$$

We simplify the discussion and discuss an isotropic material,  $\epsilon_{ij}(\omega) = \delta_{ij} \epsilon(\omega)$ . We intend to show that the real part of the susceptibility is responsible for refraction while the imaginary part causes absorption.

Consider a damped plane wave traveling in  $z$  direction:

$$E_1 = E e^{-i\omega t} e^{ink_0 z} e^{-\alpha z/2} ; E_2 = 0 ; E_3 = 0 . \quad (6.23)$$

The wave number is  $q = nk_0$  where  $k_0 = \omega/c$ .  $n$  is the refractive index,  $\alpha$  the absorption constant. Inserting (6.23) into (6.21) shows that we have guessed correctly, provided

$$\epsilon = \epsilon' + i\epsilon'' = \left( n + i \frac{\alpha}{2k_0} \right)^2 = n^2 + i \frac{n\alpha}{k_0} + \dots \quad (6.24)$$

holds true. Thus we have shown that

$$n = \sqrt{\epsilon'} \quad (6.25)$$

is the refractive index and

$$\alpha = \frac{k_0 \epsilon''}{n} \quad (6.26)$$

the absorption constant. Recall that the energy current density  $S$  is quadratic in the electromagnetic field strengths. Therefore,  $\alpha$  is indeed the power decay constant of radiation. Proving  $\epsilon'' \geq 0$  is close to proving the second law of thermodynamics. We will address this challenge in the following section.

The susceptibility is the Fourier transform of a real function, therefore  $\chi(\omega) = \chi^*(-\omega)$ . Consequently, the real part is an even, the imaginary part an odd function of angular frequency. Averaging  $\chi'(\omega)$  and  $\chi'(-\omega)$  and taking into account that  $u\chi''(u)/(u^2 - \omega^2)$  is an even function of  $u$  we arrive at

$$\chi'(\omega) = \frac{2}{\pi} \text{Pr} \int_0^\infty du \frac{u\chi''(u)}{u^2 - \omega^2} . \quad (6.27)$$

#### 6.4 Oscillator strength

We have derived in section 2 an expression for the susceptibility of elastically bound, weakly damped electrons. If there are  $N$  such electrons per unit volume resonating at frequency  $u$ , the refractive part of the susceptibility is

$$\chi'(\omega) = \frac{Ne^2}{m\epsilon_0} \frac{1}{u^2 - \omega^2} . \quad (6.28)$$

This explains why the Kramers-Kronig relation is often written in the following form:

$$n^2(\omega) = 1 + \frac{e^2}{m\epsilon_0} \text{Pr} \int_0^\infty du \frac{f(u)}{u^2 - \omega^2} . \quad (6.29)$$



$f = f(\omega)$  is the oscillator strength describing the distribution of resonance frequencies.

$$N = \int_0^\infty du f(u) \quad (6.30)$$

is the spatial density of elastically bound electrons. The oscillator strength of (6.29) is given by

$$f(\omega) = \frac{2}{\pi} \frac{m c \epsilon_0}{e^2} n(\omega) \alpha(\omega) \quad (6.31)$$

Note that the static dielectric constant is

$$\epsilon(0) = 1 + \frac{N e^2}{m \epsilon_0 \bar{\omega}^2} \quad (6.32)$$

where  $\bar{\omega}$  is an average resonance frequency defined by

$$\int_0^\infty du \frac{f(u)}{u^2} = \frac{N}{\bar{\omega}^2} \quad (6.33)$$

The integral converges because  $f(\omega)$  is proportional to  $\omega \chi'(\omega) \propto \omega^2$ . For very high frequencies (X rays) the refractive index is given by

$$n^2(\omega) = 1 - \frac{N e^2}{m \epsilon_0 \omega^2} \quad (6.34)$$

A refractive index less than 1 means that the phase velocity  $\omega/k = c/n$  is larger than  $c$ . This does not imply that X ray signals may travel faster than light. Wave packets travel with group velocity  $v = d\omega/dk$  which differs from phase velocity. The speed of a signal is yet another story.

If the angular frequency  $\omega$  lies outside an absorption band,  $f(\omega) = 0$ , the principal value operator Pr in (6.29) may be omitted, and we deduce

$$\frac{dn^2}{d\omega} = \frac{2\omega e^2}{m \epsilon_0} \int_0^\infty du \frac{f(u)}{(u^2 - \omega^2)^2} \geq 0 \quad (6.35)$$

The permittivity, or the refractive index, grows with angular frequency. This behaviour of dispersion is normal. Abnormal dispersion—the refractive index decreases with increasing frequency—is possible only within absorption bands. If  $f(\omega) > 0$ , the above argument does not hold true. Abnormal dispersion comes necessarily with large absorption.

## 7 Dissipation-fluctuation theorem

It is well known that things become simpler if one concentrates on the essentials. We shall therefore discuss the relation between dissipation and fluctuation on a very abstract level. The interaction of a light wave with matter will then serve as an example.

We discuss a system which, if unperturbed, is described by its Hamiltonian  $H$ . The system's equilibrium state is  $G \propto \exp(-\beta H)$  where  $\beta = 1/k_B T$  is short for the inverse temperature (up to the Boltzmann constant  $k_B$ ). The expectation value of an observable  $M$  in the equilibrium state is denoted by  $\langle M \rangle = \text{tr} GM$  throughout.

If the equilibrium is disturbed by a time dependent contribution

$$H_t = H - \lambda(t)V \quad , \quad (7.1)$$

the linear response, as felt by an observable  $M$ , is given by

$$\langle M \rangle_t = \langle M \rangle - \int_0^\infty d\tau \lambda(t-\tau) \Gamma(MV; \tau) \quad . \quad (7.2)$$

There is an intimate relation between response functions  $\Gamma(AB; \tau)$  and correlation functions  $K(AB; \tau)$  which is the subject of this section.

### 7.1 The Wiener-Khinchin theorem

If  $A$  denotes an observable of the system under discussion,

$$A(t) = U_{-t} A U_t \quad \text{where} \quad U_t = e^{-\frac{i}{\hbar} t H} \quad (7.3)$$

is considered to be a process. Note that the equilibrium values are constant,

$$\langle A(t) \rangle = \text{tr} G U_{-t} A U_t = \text{tr} U_t G U_{-t} A = \text{tr} G A = \langle A(0) \rangle \quad . \quad (7.4)$$

However, there will be fluctuations. We describe them by the time correlation function

$$K(AB; \tau) = \frac{\langle A(t+\tau)B(t) + B(t)A(t+\tau) \rangle}{2} - \langle A \rangle \langle B \rangle \quad . \quad (7.5)$$

Because we have chosen the symmetrized product, the correlations function of two observables  $A$  and  $B$  will always be real. Note that the time argument  $t$  is absent on the left hand side of (7.5).  $K(AB; 0)$  is the correlation proper.  $K(AA; \tau)$  is a time auto-correlation function.

Let us insert the Fourier decomposed processes,

$$A(t+\tau) = \langle A \rangle + \int \frac{d\omega}{2\pi} e^{-i\omega(t+\tau)} \hat{A}(\omega) \quad (7.6)$$

and

$$B(t) = \langle B \rangle + \int \frac{d\omega'}{2\pi} e^{i\omega't} \hat{B}^\dagger(\omega') . \quad (7.7)$$

There will be a factor  $e^{-i(\omega - \omega')t}$  leading to a dependency on  $t$  unless

$$\frac{\hat{A}(\omega)\hat{B}^\dagger(\omega') + \hat{B}^\dagger(\omega')\hat{A}(\omega)}{2} = 2\pi\delta(\omega - \omega')S(\omega) . \quad (7.8)$$

In a stationary state, like in the Gibbs state, the Fourier components of fluctuations with different frequencies are not correlated. Correlated fluctuations of different frequencies would cause beating.

The frequency dependent function  $S = S(AB; \omega)$  in (7.8) is called a spectral density. With it we may write

$$K(AB; \tau) = \int \frac{d\omega}{2\pi} e^{-i\omega\tau} S(AB; \omega) . \quad (7.9)$$

$S(AA; \omega)$ , the spectral density of an auto-correlation function  $K(AA; \tau)$  is never negative,

$$K(AA; \tau) = \int \frac{d\omega}{2\pi} e^{-i\omega\tau} S(AA; \omega) \text{ where } S(AA; \omega) \geq 0 . \quad (7.10)$$

This finding is known as the Wiener-Khintchin theorem.

## 7.2 Kubo-Martin-Schwinger formula

Let us define

$$A(z) = e^{-\frac{i}{\hbar}zH} A e^{\frac{i}{\hbar}zH} \quad (7.11)$$

for  $z \in \mathbb{C}$ .

We now exploit the fact that both the Gibbs state and the time translation operators are exponential functions of the energy:

$$A(z) e^{-\beta H} = e^{-\beta H} e^{\beta H} A(z) e^{-\beta H} , \quad (7.12)$$

i.e.  $A(z)G = GA(z - i\hbar\beta)$ . We multiply from the right by  $B$  and apply the trace operator. The result

$$\langle BA(z) \rangle = \langle A(z - i\hbar\beta)B \rangle \quad (7.13)$$

is the famous Kubo-Martin-Schwinger, or KMS formula.

### 7.3 Response and correlation

Note the formal similarity between the response function

$$\Gamma(AB; \tau) = \left\langle \frac{i}{\hbar} [A(\tau), B] \right\rangle \quad (7.14)$$

and the correlation function

$$K(AB; \tau) = \frac{\langle A(\tau)B + BA(\tau) \rangle}{2} - \langle A \rangle \langle B \rangle . \quad (7.15)$$

The difference is essentially the difference between a commutator and an anti-commutator.

We therefore investigate the product,

$$\phi(\tau) = \langle A(\tau)B \rangle - \langle A \rangle \langle B \rangle . \quad (7.16)$$

Its Fourier transform is

$$\hat{\phi}(\omega) = \int d\tau e^{i\omega\tau} \phi(\tau) . \quad (7.17)$$

Let us now discuss the function

$$f(z) = \int \frac{d\omega}{2\pi} e^{-i\omega z} \hat{\phi}(\omega) . \quad (7.18)$$

It can be shown that this function is analytic within a large enough strip of the complex  $z$ -plane around the real axis. On the real axis we clearly have  $f(\tau) = \phi(\tau)$ . Indeed, function  $f$  is the analytic continuation into the complex plane of function  $\phi$ .

With (7.11) we may work out

$$g(z) = \langle A(z)B \rangle - \langle A \rangle \langle B \rangle \quad (7.19)$$

which is analytic in a sufficiently broad strip around the real axis. On the real axis we have  $g(\tau) = f(\tau)$ . Therefore,  $g(z)$  and  $f(z)$  coincide everywhere.

Applying the KMS formula yields

$$\langle BA(\tau) \rangle - \langle A \rangle \langle B \rangle = f(\tau - i\hbar\beta) . \quad (7.20)$$

One should compare this with

$$\langle A(\tau)B \rangle - \langle A \rangle \langle B \rangle = f(\tau) . \quad (7.21)$$

### 7.4 The Callen-Welton theorem

The response function can now be written as

$$\Gamma(AB; \tau) = \frac{i}{\hbar} \{f(\tau) - f(\tau - i\hbar\beta)\} . \quad (7.22)$$

For the time correlation function we obtain

$$K(AB; \tau) = \frac{1}{2} \{f(\tau) + f(\tau - i\hbar\beta)\} . \quad (7.23)$$

We insert the representation (7.18) of  $f$ ,

$$\Gamma(AB; \tau) = \frac{i}{\hbar} \int \frac{d\omega}{2\pi} e^{-i\omega\tau} \hat{\phi}(\omega) \left\{ 1 - e^{-\beta\hbar\omega} \right\} , \quad (7.24)$$

$$K(AB; \tau) = \frac{1}{2} \int \frac{d\omega}{2\pi} e^{-i\omega\tau} \hat{\phi}(\omega) \left\{ 1 + e^{-\beta\hbar\omega} \right\} . \quad (7.25)$$

One can read off immediately the Fourier transforms, and eliminating  $\hat{\phi}$  results in

$$\hat{\Gamma}(AB; \omega) = 2 \frac{i}{\hbar} S(AB; \omega) \tanh \frac{\beta\hbar\omega}{2} . \quad (7.26)$$

We are more interested in the (generalized) susceptibility

$$\gamma(AB; \omega) = \int_0^\infty d\tau e^{i\omega\tau} \Gamma(AB; \tau) . \quad (7.27)$$

Recall the result

$$\gamma(AB; \omega) - \gamma(BA; \omega)^* = \hat{\Gamma}(AB; \omega) \quad (7.28)$$

of section 6 where  $A$  was  $P_i$  and  $B = P_j$ .

Combining (7.26) and (7.28) results in

$$\frac{\gamma(AB; \omega) - \gamma(BA; \omega)^*}{2i} = S(AB; \omega) \frac{1}{\hbar} \tanh \frac{\beta\hbar\omega}{2} . \quad (7.29)$$

This is the famous fluctuation-dissipation theorem of Callen and Welton.

### 7.5 Energy dissipation

Let us discuss a process  $W_t$  with the initial condition  $W_{-\infty} = G \propto e^{-\beta H}$ . This process is driven by the time dependent Hamiltonian

$$H_t = H - \sum_r \lambda_r(t) V_r , \quad (7.30)$$

and we assume  $\lambda_r(t) \rightarrow 0$  for  $|t| \rightarrow \infty$ . During the small time span  $dt$  the following amount of work

$$dA = - \sum d\lambda_r \langle V_r \rangle_t = - \sum dt \dot{\lambda}_r(t) \langle V_r \rangle_t \quad (7.31)$$

is spent on the system, where  $\langle V_r \rangle_t = \text{tr } W_t V_r$ . This follows from the first law of thermodynamics. The total work spent on the system is

$$A = - \sum_r \int dt \dot{\lambda}_r(t) \langle V_r \rangle_t . \quad (7.32)$$

We assume that the external parameters are always small, so that the linear approximation to the response is sufficient:

$$\langle V_r \rangle_t = \langle V_r \rangle + \sum_s \int_0^\infty d\tau \Gamma_{rs}(\tau) \lambda_s(t - \tau) . \quad (7.33)$$

The response functions are

$$\Gamma_{rs}(\tau) = \Gamma(V_r V_s; \tau) = \left\langle \frac{i}{\hbar} [V_r(\tau), V_s(0)] \right\rangle . \quad (7.34)$$

The constant terms  $\langle V_r \rangle$  do not contribute, and we may write

$$A = - \sum_{rs} \int dt \int d\tau \dot{\lambda}_r(t) \lambda_s(t - \tau) \theta(\tau) \Gamma_{rs}(\tau) . \quad (7.35)$$

This is an expression of type

$$\int dt' \int dt'' f(t') g(t' - t'') h(t'') = \int \frac{d\omega}{2\pi} \hat{f}(\omega)^* \hat{g}(\omega) \hat{h}(\omega) , \quad (7.36)$$

and we may write

$$A = - \sum_{rs} \int \frac{d\omega}{2\pi} i\omega \hat{\lambda}_r(\omega)^* \chi_{rs}(\omega) \hat{\lambda}_s(\omega) . \quad (7.37)$$

Note that

$$\chi_{rs}(\omega) = \int d\tau e^{i\omega\tau} \theta(\tau) \Gamma_{rs}(\tau) \quad (7.38)$$

are generalized susceptibilities.

Complex conjugating (7.37) and interchanging the summation indices  $r, s$  will not change the value of  $A$ ,

$$A = - \sum_{sr} \int \frac{d\omega}{2\pi} i\omega \hat{\lambda}_s(\omega) \chi_{sr}^*(\omega) \hat{\lambda}_r^*(\omega) , \quad (7.39)$$

and averaging (7.37) and (7.39) results in

$$A = \sum_{rs} \int \frac{\omega d\omega}{2\pi} \hat{\lambda}_r(\omega)^* \frac{\chi_{rs}(\omega) - \chi_{sr}(\omega)^*}{2i} \hat{\lambda}_s(\omega) . \quad (7.40)$$

With the dissipation-fluctuation theorem (7.29) we finally arrive at

$$A = \frac{\beta}{2} \int \frac{\omega^2 d\omega}{2\pi} q(\beta\hbar\omega) \sum_{rs} \hat{\lambda}_r(\omega)^* S_{rs}(\omega) \hat{\lambda}_s(\omega) \quad (7.41)$$

where

$$q(x) = \frac{2}{x} \tanh \frac{x}{2} \quad (7.42)$$

is a quantum mechanical correction. By the Wiener-Khintchin theorem the matrix  $S_{rs} = S_{rs}(\omega)$  of spectral densities is non-negative.

We conclude that it is impossible to perturb an equilibrium state in such a way that the system extracts heat from its environment and delivers work:  $A \geq 0$ . This statement is an alternative formulation of the second law of thermodynamics. We have proven it here for small perturbations of the equilibrium by rapidly oscillating external parameters.

A more prosaic formulation reads: the absorptive part of the susceptibility truly causes absorption of energy.

## 8 Onsager relations

If the equilibrium is perturbed by more than one driving force, the generalized susceptibilities  $\chi_{rs}(\omega)$  form a matrix. We have shown in section 7 that the imaginary, or absorptive part  $\chi_{rs}(\omega) - \chi_{sr}(\omega)^*$  is non-negative and proportional to the matrix of spectral densities. This was the subject of the dissipation-fluctuation theorem.

In this section we discuss symmetry properties of the susceptibility matrix.

### 8.1 Symmetry of static susceptibilities

Let us first discuss the symmetry properties for adiabatic processes. Let  $\lambda = \lambda_1, \lambda_2, \dots$  denote external parameters or deviations thereof such that

$$H(\lambda) = H - \sum_r \lambda_r V_r \quad (8.1)$$

is the relevant Hamiltonian. If the external parameters change slowly, the state  $W$  of the system will always be the equilibrium state to the current external parameters  $\lambda$ . The free energy is given by

$$F(\lambda, \beta) = -\frac{1}{\beta} \ln \text{tr} e^{-\beta H(\lambda)} \quad (8.2)$$

With  $\langle \dots \rangle$  as expectation value in the Gibbs state to  $H(0)$  and  $\langle \dots \rangle_\lambda$  to  $H(\lambda)$  we find

$$\langle V_r \rangle_\lambda = \langle V_r \rangle + \sum_s \lambda_s \left. \frac{\partial \langle V_r \rangle_\lambda}{\partial \lambda_s} \right|_{\lambda=0} \quad (8.3)$$

Comparing with (7.33) we conclude

$$\chi_{rs}(0) = \int_0^\infty d\tau \Gamma_{rs}(\tau) = -\frac{\partial^2 F(\lambda, \beta)}{\partial \lambda_s \partial \lambda_r} \quad (8.4)$$

It follows immediately that

$$\chi_{rs}(0) = \chi_{sr}(0) \quad (8.5)$$

holds true. Can this symmetry be generalized to fast processes? Almost, as we shall see.

### 8.2 Time reversal

To each linear operator  $A$  we assign a time-reversed operator  $A^*$  by

$$(A\phi)^* = A^*\phi^* \quad (8.6)$$



where  $\phi = \phi(x_1, x_2, \dots)$  is an arbitrary wave function depending on the positions of the particles. Let us ignore spin at this point. As usual,  $*$  denotes complex conjugation.

Note that the mapping  $A \rightarrow A^*$  is anti-linear in the sense that  $A + B$  map to  $A^* + B^*$ , but  $zA$  becomes  $z^*A^*$

A position operator  $\mathbf{x}$  amounts to the multiplication of the wave function by its argument, which is real. Therefore,  $\mathbf{x}^* = \mathbf{x}$ . Momentum operators are represented by  $\mathbf{p} = -i\hbar\nabla$ , therefore  $\mathbf{p}^* = -\mathbf{p}$ . This is the reason why the time-reversal is sometimes called momentum reversal. By the way, angular momenta change their sign at timer reversal as well.

If  $\phi$  is an eigenfunction of  $A$  with eigenvalue  $a$ , then  $\phi^*$  is an eigenfunction of  $A^*$  with eigenvalue  $a^*$ . Hence, if  $M$  is an observable, so is  $M^*$ , and if  $W$  represents a mixed state, so does  $W^*$ . Observables are characterized by real eigenvalues. States also have real eigenvalues which are probabilities. It is a simple exercise to prove the expectation value of an observable in a state coincides with the expectation value of the time reversed observable in the time reversed state,

$$\text{tr} WM = \text{tr} W^*M^* . \quad (8.7)$$

An observable is of parity  $\eta$  (with respect to time reversal) if  $M^* = \eta M$  holds true. Because of  $M^{**} = M$  only  $\eta = \pm 1$  are possible. Position operators have even, momentum or angular momentum operators odd parity.

Ordinarily, the Hamiltonian has even parity. However, if there is an external quasi-static magnetic induction field  $\bar{\mathbf{B}}$ , there is a contribution  $-\sum \mu_i \bar{B}_i$ , the magnetic dipole interaction. Since the magnetic momentum is proportional to an angular momentum, which has odd time reversal parity, we conclude

$$H(\bar{\mathbf{B}})^* = H(-\bar{\mathbf{B}}) . \quad (8.8)$$

The external magnetic induction field has to be reversed in order to guarantee even parity of the Hamiltonian.

Now, the Gibbs state depends, among other external parameters, upon the quasi-static magnetic induction applied to the system,  $G = G(\bar{\mathbf{B}})$ . We conclude

$$G(\bar{\mathbf{B}})^* = G(-\bar{\mathbf{B}}) . \quad (8.9)$$

The time translation operator is

$$U_t(\bar{\mathbf{B}}) = e^{-\frac{i}{\hbar} t H(\bar{\mathbf{B}})} , \quad (8.10)$$

and we easily work out

$$U_t(\bar{\mathbf{B}})^* = U_{-t}(-\bar{\mathbf{B}}) . \quad (8.11)$$

This explains why we speak of time reversal. The time reversed time translation operator  $U_t^*$  translates by the negative time span,  $U_{-t}$ . However,  $\bar{\mathbf{B}} \rightarrow -\bar{\mathbf{B}}$  has to be observed.

### 8.3 Onsager theorem

Let us come back to the original situation that there is a Hamiltonian with a time-dependent perturbation,

$$H_t = H(\bar{B}) - \sum_s \lambda_s(t) V_s . \quad (8.12)$$

For the expectation values of the perturbing observables we have found

$$\text{tr } W_t V_r = \text{tr } G(\bar{B}) V_r + \int_0^\infty d\tau \Gamma_{rs}(\bar{B}; \tau) \lambda_s(t - \tau) , \quad (8.13)$$

where

$$\Gamma_{rs}(\bar{B}; \tau) = \text{tr } G(\bar{B}) \frac{i}{\hbar} [U_{-\tau}(\bar{B}) V_r U_\tau(\bar{B}), V_s] . \quad (8.14)$$

The latter expression may be rewritten as

$$\text{tr } G(\bar{B})^* \frac{i}{\hbar} [U_{-\tau}(\bar{B}) V_r U_\tau(\bar{B}), V_s]^* \quad (8.15)$$

which becomes

$$- \text{tr } G(-\bar{B}) \frac{i}{\hbar} [U_\tau(-\bar{B}) V_r^* U_{-\tau}(\bar{B}), V_s^*] . \quad (8.16)$$

We assume that the  $V_r$  observables have parities  $\eta_r$  with respect to time reversal. Thus we may write

$$-\eta_r \eta_s \text{tr } G(-\bar{B}) \frac{i}{\hbar} [U_\tau(-\bar{B}) V_r U_{-\tau}(\bar{B}), V_s] \quad (8.17)$$

holds. By shifting the entire commutator in time by  $\tau$  (which is allowed because  $G$  is stationary) we arrive at

$$-\eta_r \eta_s \text{tr } G(-\bar{B}) \frac{i}{\hbar} [V_r(\bar{B}), U_{-\tau} V_s U_\tau(-\bar{B})] , \quad (8.18)$$

and reverting the commutator finally yields

$$\Gamma_{rs}(\bar{B}; \tau) = \eta_r \eta_s \Gamma_{sr}(-\bar{B}; \tau) . \quad (8.19)$$

This symmetry is maintained if (8.19) is Fourier transformed over positive time spans  $\tau$  resulting in a symmetry relation for the (generalized) susceptibilities:

$$\chi_{rs}(\bar{B}; \omega) = \eta_r \eta_s \chi_{sr}(-\bar{B}; \omega) . \quad (8.20)$$

(8.20) is an Onsager relation. It applies in particular to the dielectric susceptibility where  $\eta_r = \eta_s = 1$ .

By the way, (8.20) and (8.5) do not contradict each other.  $\eta_r \neq \eta_s$  will imply  $\chi_{rs}(0; 0) = 0$ .

### 8.4 Onsager relation for kinetic coefficients

Let us define the flux of  $V$  by

$$J = \dot{V} = \frac{i}{\hbar} [H, V] . \quad (8.21)$$

In the case of electric polarization  $P_r(x)$ ,

$$J_r = \sum_a q_a \dot{\mathbf{x}}_a \delta^3(x - \mathbf{x}_a) \quad (8.22)$$

are the three components of the electric current density.

If  $V$  has parity  $\eta$  with respect to time reversal, then  $J$  has parity  $-\eta$ .

Because the Gibbs state is stationary, the equilibrium expectation value of fluxes vanishes. The expectation value  $J(t) = \text{tr } W_t J$  in the perturbed state is also called a flux. Fluxes exist because the equilibrium is perturbed.

With

$$\Gamma(J_r V_s; \tau) = \left\langle \frac{i}{\hbar} [\dot{V}_r(\tau), V_s] \right\rangle = \dot{I}_{sr}(\tau) \quad (8.23)$$

we conclude

$$J_r(t) = \sum_s \int_0^\infty d\tau \dot{I}_{rs}(\tau) \lambda_s(t - \tau) . \quad (8.24)$$

Fourier transforming results in

$$\hat{J}_r(\omega) = \sum_s \sigma_{rs}(\omega) \hat{\lambda}_s(\omega) , \quad (8.25)$$

where

$$\sigma_{rs}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} \dot{I}_{rs}(\tau) \quad (8.26)$$

are kinetic coefficients. Differentiating (8.19) and inserting into (8.26) leads to

$$\sigma_{rs}(\bar{B}; \omega) = \eta_r \eta_s \sigma_{sr}(-\bar{B}; \omega) . \quad (8.27)$$

This symmetry relation for kinetic coefficients was derived already in 1931 by Onsager, although for stationary currents only ( $\omega = 0$ ). His reasoning was different and, from today's point of view, questionable. However, Onsager also considered other causes of irreversible effects like gradients of temperature and chemical potential.

### 8.5 Electrical conductivity and Hall effect

If the equilibrium state of matter is disturbed by an electric field, then

$$\hat{J}_i(\omega) = \sum_j \sigma_{ij}(\bar{B}; \omega) \hat{E}_j(\omega) . \quad (8.28)$$

This is Ohm's law.  $\sigma_{ij}$  is the conductivity tensor which may depend on an external magnetic field. For a sufficiently weak magnetic field and for an isotropic material we may expand according to

$$\sigma_{ij}(\bar{B}; \omega) = \sigma(\omega) \delta_{ij} + h(\omega) \sum_k \epsilon_{ijk} \bar{B}_k + \dots . \quad (8.29)$$

The first term describes electric conduction in the absence of a magnetic field. The second term must be antisymmetric in  $i$  and  $j$  because it is linear in  $\bar{B}$ . There is a current contribution perpendicular to the driving electric field strength  $\mathbf{E}$  and perpendicular to the quasi-static induction  $\bar{\mathbf{B}}$ .

## 9 Electro- and magneto-optic effects

Let us recall the expression

$$\chi_{ij}(\omega) = \frac{1}{\epsilon_0} \int_0^\infty d\tau e^{i\omega\tau} \int d^3\xi \operatorname{tr} G \frac{i}{\hbar} [P_i(\tau, \xi), P_j(0, 0)] \quad (9.1)$$

for the dielectric susceptibility tensor.

$$P_i(\tau, \xi) = \sum_a q_a \mathbf{x}_a \delta^3(\mathbf{x}_a - \xi) \quad (9.2)$$

is the polarization at location  $\xi$ , translated by a time span  $\tau$ . The susceptibilities are integrals over expectation values in the Gibbs, or equilibrium state. Therefore, they depend on all parameters which describe the thermal equilibrium state: composition of matter, temperature, external quasi-static electric and magnetic fields, stress, and so forth.

We will concentrate on quasi-static external electric and magnetic fields  $\mathbf{E}$  and  $\mathbf{B}$ , respectively.

A systematic power series expansion up to second order reads

$$\chi_{ij}(\mathbf{E}, \mathbf{B}) = \chi_{ij}^{00} \quad (9.3)$$

$$+ \chi_{ijk}^{10} E_k \quad (9.4)$$

$$+ \chi_{ijk}^{01} B_k \quad (9.5)$$

$$+ \chi_{ijkl}^{20} E_k E_l \quad (9.6)$$

$$+ \chi_{ijkl}^{11} E_k B_l \quad (9.7)$$

$$+ \chi_{ijkl}^{02} B_k B_l \quad (9.8)$$

$$+ \dots$$

Recall that we speak of the Hermitian refractive part,

$$\chi_{ij}(\mathbf{E}, \mathbf{B}) = \chi_{ji}^*(\mathbf{E}, \mathbf{B}) \quad (9.9)$$

and that Onsager's relation demands

$$\chi_{ij}(\mathbf{E}, \mathbf{B}) = \chi_{ji}(\mathbf{E}, -\mathbf{B}) \quad (9.10)$$

The same is true for the permittivity tensor  $\epsilon_{ij} = \delta_{ij} + \chi_{ij}$ .

### 9.1 Crystal optics

We assume a real symmetric, but otherwise arbitrary permittivity tensor. The medium is assumed to be non-magnetic. Let us look for plane wave solutions:

$$\mathbf{F}(t, \mathbf{x}) = \mathbf{f} e^{-i\omega t} e^{i n k_0 \mathbf{w} \cdot \mathbf{x}} \quad (9.11)$$

$\mathbf{F}$  is any vector field.  $\mathbf{w}$ , a unit vector, defines the direction of propagation,  $k_0$  is short for  $\omega/c$ , and  $n$  denotes the refractive index.

Maxwell's equations read

$$c\mathbf{b} = -n\mathbf{w} \times (\epsilon\mathbf{e}) ; \mathbf{e} = n\mathbf{w} \times (c\mathbf{b}) . \quad (9.12)$$

Note that the remaining equations  $\mathbf{w} \cdot (\epsilon\mathbf{e}) = 0$  as well as  $\mathbf{w} \cdot \mathbf{b} = 0$  are automatically fulfilled: the dielectric displacement  $\mathbf{D}$  and the induction field  $\mathbf{B}$  are divergence free.  $c$  is the speed of light in vacuum.

For a prescribed direction  $\mathbf{w}$  of propagation, (8.2) may be understood as an eigenvalue problem.  $\mathbf{w} \times \dots$  is a linear operator described by the matrix

$$W = \begin{pmatrix} 0 & w_3 & -w_2 \\ -w_3 & 0 & w_1 \\ w_2 & -w_1 & 0 \end{pmatrix} . \quad (9.13)$$

Eliminating the induction result in

$$\epsilon^{-1} W^2 \mathbf{e} = n^{-2} \mathbf{e} . \quad (9.14)$$

Because of  $W\mathbf{w} = 0$ , there is one unphysical solution, namely  $\mathbf{e} = \mathbf{w}$ , with  $n^{-2} = 0$ . The remaining two eigenvectors describe the polarization of allowed propagation modes, the eigenvalues  $n^{-2}$  defining the respective refractive indices.

**Optically isotropic media** The three eigenvalues of the susceptibility coincide,  $\chi_{ij}^{00} = \chi\delta_{ij}$ . Amorphous substances, such as glass, and crystals with cubic symmetry, such as NaCl, are examples. All transversely polarized plain waves are eigenmodes, the refractive index being  $n = \sqrt{1 + \chi}$ .

**Optically uniaxial crystals** If two eigenvalues of  $\epsilon_{ij}^{00}$  coincide, but differ from the third, one has a preferred axis and, orthogonal to it, a preferred plane. If the polarization vector lies in the preferred plane, the beam propagates with the ordinary main refractive index<sup>6</sup>  $n^o$ , the square root of the doubly occurring eigenvalue. If the beam is polarized in the preferred axis, one speaks of the extraordinary main refractive index  $n^e$ . The preferred axis is an optical axis in the following sense: if light propagates along it, the refractive index does not depend on polarization.

If a light beam enters an optically uniaxial crystal at an arbitrary angle, it splits into an ordinary<sup>7</sup> and an extraordinary beam which travel with different refractive indices. One therefore speaks of double refraction, or birefringence. LiNbO<sub>3</sub> is a well-known and extensively studied birefringent crystal.

<sup>6</sup>The refractive index  $n$  is a property of the wave. With  $k_0 = \omega/c$  and  $\mathbf{w}$  as propagation direction, the wave vector is  $\mathbf{q} = nk_0\mathbf{w}$ .

<sup>7</sup>ordinary, because it propagates in the plane of incidence spanned by the incoming beam and the surface normal

**Optically biaxial crystals** If the symmetry of a crystal is low enough, all three eigenvalues of the susceptibility tensor  $\chi_{ij}^{00}$  may be different. One can, however, demonstrate that there are two optical axes such that beams, when traveling along it, have a polarization independent refractive index. Therefore, crystals with three different susceptibility eigenvalues are called optically biaxial. They are birefringent as well. An incident beam splits into two beams which propagate with different refractive indices. However, in the general case, none of them is ordinary in the sense that it remains in the plane of incidence.

## 9.2 Pockels effect

The addition  $\chi_{ijk}^{10} E_k$  is linear in the strength of an external electric field. (9.9) and (9.10) require  $\chi_{ijk}^{10}$  to be a real third-rank tensor which has to be symmetric in the first two indices.

Note that space inversion  $t \rightarrow t$  and  $\mathbf{x} \rightarrow -\mathbf{x}$  is a symmetry of Maxwell's equations if  $\mathbf{E} \rightarrow -\mathbf{E}$  and  $\mathbf{B} \rightarrow \mathbf{B}$ . Put otherwise, the electric field strength is a polar, the magnetic field strength an axial vector. If the Gibbs state is invariant with respect to space inversion,  $\chi_{ijk}^{10}$  will acquire a minus sign, it must coincide with its negative, hence vanish. We conclude that a third rank tensor is possible only for crystals which do not have an inversion center. If there is a location (at  $\mathbf{x} = 0$ ) such that  $\mathbf{x} \rightarrow -\mathbf{x}$  is a symmetry, then  $\chi_{ijk}^{10}$  necessarily vanishes.

Lithium niobate<sup>8</sup>  $\text{LiNbO}_3$  may serve as an example. There is an  $xy$ -plane with a  $120^\circ$  symmetry and mirror symmetry  $x \rightarrow -x$ . The  $c$ -axis, orthogonal to this plane, has a preferred direction. After all,  $\text{LiNbO}_3$  is ferro-electric. Consequently, there are four different third-rank tensors which fulfill all requirements. We have deferred a detailed discussion to appendix B.

The Pockels effect, the dependence of the refractive index on the first power of a quasi-static electric field strength, allows to switch and modulate light.

## 9.3 Faraday effect

Faraday has discovered that a magnetic field may affect the propagation of light. The contribution  $\chi_{ijk}^{01} B_k$  to the susceptibility must be Hermitian and symmetric if  $\mathbf{B}$  is reversed. Consequently,  $\chi_{ijk}^{01}$  is to be purely imaginary and antisymmetric in  $i$  and  $j$ .

To be specific, let us discuss yttrium iron garnet (YIG), a complicated artificial crystal which is transparent in the micrometer wavelength region and ferri-magnetic at the same time. There is a contribution

$$\chi_{ijk}^{01} B_k = iK \epsilon_{ijk} M_k \quad (9.15)$$

to the susceptibility. Because YIG is ferri-magnetic, it is customary to refer to the magnetization  $\mathbf{M}$  instead of  $\mathbf{B}$ .

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<sup>8</sup>at room temperature of 3m-symmetry

Let us discuss a situation where a wave propagates along the direction of magnetization, the  $z$ -axis, say. With  $k_0 = \omega/c$  and  $\mathbf{k} = nk_0(0, 0, 1)$  we have to solve

$$-\mathbf{k} \times \mathbf{k} \times \mathbf{E} = k_0^2 \epsilon \mathbf{E} \quad (9.16)$$

where

$$\epsilon = \begin{pmatrix} \epsilon & iKM & 0 \\ -iKM & \epsilon & 0 \\ 0 & 0 & \epsilon \end{pmatrix}. \quad (9.17)$$

With

$$\hat{\mathbf{e}}_L = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix} \quad \text{and} \quad \hat{\mathbf{e}}_R = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \quad (9.18)$$

we have made out solutions which describe left and right hand circularly polarized light,

$$\mathbf{E}_{L,R} = E \hat{\mathbf{e}}_{L,R} e^{-i\omega t} e^{in_{L,R}k_0 z} \quad (9.19)$$

Their refractive indices differ:

$$n_L^2 = \epsilon + KM \quad \text{and} \quad n_R^2 = \epsilon - KM \quad (9.20)$$

If a linearly polarized plane wave enters a crystal with linear magneto-optic effect, it splits into left and right hand circularly polarized waves. These waves travel with slightly different phase velocity. When exiting the crystal, the two waves recombine again to a linearly polarized wave. However, the direction of polarization is rotated by an angle  $\Theta \ell$ , where  $\ell$  is the path length through the magneto-optic medium. The specific Faraday rotation constant is given by

$$\Theta = \frac{2\pi KM}{\lambda 2n}, \quad (9.21)$$

where  $n = \sqrt{\epsilon}$  is the average refractive index.

The Faraday effect distinguishes between forward and backward propagation of light and allows to build an optical isolator.

#### 9.4 Kerr effect

Unlike the Pockels effect, which is linear in the external electric field strength and requires a medium without inversion center, the Kerr effect is usually much weaker, because of second order. It is a property even of isotropic media since

$$\chi_{ijkl}^{(2)} \propto \delta_{ij} \delta_{kl} \quad (9.22)$$

fulfills all symmetry requirements: real, symmetric in the first pair of indices, symmetric in the second pair of indices. (9.18) amounts to a shift of the refractive index by a term proportional to  $|\mathbf{E}|^2$ .



### 9.5 Magneto-electric effect

There is no accepted name for a contribution  $\chi_{ijk\ell}^{11} E_k B_\ell$  to the susceptibility tensor. One may speak of a linear dependence of the Pockels effect on an external magnetic field. One may likewise say that the Faraday effect depends linearly on an external electric field. The  $\chi_{ijk\ell}^{11}$  must be purely imaginary and antisymmetric in the first pair of indices. The crystal should be ferro- or ferri-magnetic, transparent, and must not have an inversion center.

### 9.6 Cotton-Mouton effect

The Cotton-Mouton effect, a permittivity shift which is of second order in the magnetic field, is rather weak for para-magnetic material. However, if it occurs in a ferri- or ferro-magnetic substance, it may be strong. A contribution  $\chi_{ijk\ell}^{02} \propto \delta_{ij} \delta_{k\ell}$  will change  $\epsilon$  by a term which is proportional to  $|\mathbf{M}|^2$  and will escape attention. The Cotton-Mouton effect is reciprocal, unlike the Faraday effect it does not distinguish between forward and backward propagation.

## 10 Spatial dispersion

Recall the definition of the susceptibility tensor:

$$\chi_{ij}(\omega, \mathbf{q}) = \frac{1}{\epsilon_0} \int_0^\infty d\tau e^{i\omega\tau} \int d^3\xi e^{-i\mathbf{q}\cdot\boldsymbol{\xi}} \Gamma_{ij}(\tau, \boldsymbol{\xi}) \quad (10.1)$$

where

$$\Gamma_{ij}(\tau, \boldsymbol{\xi}) = \text{tr} G \frac{i}{\hbar} [P_i(\tau, \boldsymbol{\xi}), P_j(0, 0)] \quad (10.2)$$

The polarization—as an operator—is defined by

$$P_i(\mathbf{x}) = \sum_a q_a x_i \delta^3(\mathbf{x}_a - \mathbf{x}) \quad (10.3)$$

The sum extends over all charged particles, and  $\mathbf{x}_a$  is particle's  $a$  position, likewise an observable. The time shift is accomplished by the unperturbed Hamiltonian  $H$ . The entire Hamiltonian is

$$H_t = H - \int d^3x P_j(\mathbf{x}) E_j(t, \mathbf{x}) \quad (10.4)$$

where the external electric field may depend on time.

The response functions  $\Gamma_{ij}$  appear in

$$\text{tr} W_t P_i(\mathbf{x}) = \int_0^\infty d\tau \int d^3\xi \Gamma_{ij}(\tau, \boldsymbol{\xi}) E_j(t - \tau, \mathbf{x} - \boldsymbol{\xi}) \quad (10.5)$$

where  $W = W_t$  is the disturbed state, and the right hand side refers to the lowest order approximation<sup>9</sup>.

Fourier transforming  $\mathbf{E} = \mathbf{E}(t, \mathbf{x})$  and the left hand side of (10.5) results in

$$\hat{P}_i(\omega, \mathbf{q}) = \chi_{ij}(\omega, \mathbf{q}) \hat{E}_j(\omega, \mathbf{q}) \quad (10.6)$$

### 10.1 Dispersion relation

So far we have argued that the dependence of  $\chi_{ij}(\omega, \mathbf{q})$  on the wave vector  $\mathbf{q}$  is so weak that the value at  $\mathbf{q} = 0$  suffices. Interactions in a solid spread out with the speed of sound while the electromagnetic field is governed by the speed of light, and both differ by orders of magnitude. Still, there are certain effects where spatial dispersion—the dependency of the susceptibility on the wave vector—has to be taken into account.

The arguments  $\omega$  and  $\mathbf{q}$  for  $\hat{\mathbf{E}} = \hat{\mathbf{E}}(\omega, \mathbf{q})$  are not independent. After all, the electric field has to obey Maxwell's equations which, for this purpose, read

$$(q^2 \delta_{ij} - q_i q_j) \hat{E}_j = \left(\frac{\omega}{c}\right)^2 (\delta_{ij} + \chi_{ij}) \hat{E}_j \quad (10.7)$$

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<sup>9</sup>Ferro-electric materials contain an additional static contribution  $P_i^* = \text{tr} G P_i$

Recall that both  $\hat{E}_j$  and  $\chi_{ij}$  in (10.7) depend on  $\omega$  and  $\mathbf{q}$ . The wave equation may be viewed as an eigenvalue equation:  $\mathbf{q}$  given, find an  $\omega$  such that (10.7) is satisfied for a non-trivial eigenvector  $\hat{\mathbf{E}}$ .

The relation between wave vectors  $\mathbf{q}$  and angular frequency  $\omega$  is a dispersion relation. Since  $\omega$  enters (10.7) twice, as a factor on the right hand side and as an argument of the susceptibility, the eigenvalue problem is non-linear.

This complication is seldom realized because the approximation  $\chi_{ij}(\omega, \mathbf{q}) \approx \chi_{ij}(\omega, 0)$  is used. The angular frequency then may be considered as an independent variable, and the refractive index squared<sup>10</sup> appears to be the eigenvalue to be determined.

## 10.2 Optical activity

To take spatial dispersion into account, let us expand the susceptibility as

$$\chi_{ij}(\omega, \mathbf{q}) = \chi_{ij}(\omega) + \chi_{ijk}^{\text{oa}} q_k + \dots \quad (10.8)$$

The additional contribution  $\Delta\chi_{ij}^{\text{oa}} = \chi_{ijk}^{\text{oa}} q_k$  causes optical activity by traditional terminology.

It is not difficult to show that invariance with respect to time reversal<sup>11</sup> results in

$$\Gamma_{ij}(\tau, \boldsymbol{\xi}) = \Gamma_{ji}(\tau, -\boldsymbol{\xi}) \quad (10.9)$$

which, in turn, implies

$$\chi_{ij}(\omega, \mathbf{q}) = \chi_{ji}(\omega, -\mathbf{q}) \quad (10.10)$$

We conclude that  $\chi_{ijk}^{\text{oa}}$  is purely imaginary and antisymmetric in the first two indices, because the susceptibility must be Hermitian and because of (10.10). We write<sup>12</sup>

$$\Delta\chi_{ij}^{\text{oa}} = i\epsilon_{ijk} g_k \quad \text{with } g_k = G_{k\ell} q_\ell \quad (10.11)$$

$\mathbf{g}$  is the gyration vector which depends linearly on the wave vector.

With respect to space inversion,  $G_{k\ell}$  must be a rank 2 pseudo-tensor because  $\epsilon_{ijk}$  is a rank 3 pseudo-tensor while the susceptibility and the wave vector are normal tensors of rank 2 and 1, respectively.

Only crystals with a built-in screw sense can be optically active. Quartz is an example, or a solution of natural dextrose. Note that the expression

$$\Delta\chi_{ij}^{\text{fe}} = iK\epsilon_{ijk} M_k \quad (10.12)$$

<sup>10</sup>Recall  $|\mathbf{q}| = n\omega/c$  where  $n$  is the refractive index.

<sup>11</sup>in the absence of magnetic fields

<sup>12</sup> $\epsilon_{ijk}$  is the total antisymmetric Levi-Civita symbol, a rank 3 pseudo-tensor with respect to space inversion

which causes the Faraday effect, has the same structure. In full generality, also the Faraday effect should be described by a gyration vector which depends linearly on the magnetization vector. However, since the magnetization is a pseudo-vector, the tensor  $G$  in  $g_k = G_{k\ell}M_\ell$  is an ordinary rank 2 tensor, such as  $\delta_{k\ell}$ .

Optical activity results in the rotation of the polarization vector, either to the left or to the right<sup>13</sup>. Also  $K$  in (10.12) can be positive or negative. The principal difference between the Faraday effect and optical activity is the following. If a wave passes the medium twice, forward and backward, the Faraday rotations add, the rotation of the polarization vector, as caused by optical activity, is reverted. Optical activity is a reciprocal effect.

The fact that all plants produce glucose in its optically right active form (dextrose) is very astonishing. Artificial glucose consists of equal amounts of left and right optically active molecules. One molecule is the mirror image of the other form, and no chemical mechanism is known which prefers right-handedness over left-handedness. May it be that all plants stem from one and the same mother plant?

As for quartz, both forms occur in nature. The crystal growth mechanism is such that entire crystals are optically either left or right active (although there are twins).

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<sup>13</sup>Right is clockwise as seen by an observer facing the light source.

## 11 Non-linear response

Denote by  $H$  the Hamiltonian of the unperturbed system. The time translation operator associated with it is

$$U_t = e^{-\frac{i}{\hbar}tH} \quad , \quad (11.1)$$

as derived in section 4. A time translated operator  $A$  is denoted by

$$A(t) = U_{-t}AU_t \quad . \quad (11.2)$$

We want to solve the following Schrödinger equation for the system's state  $W_t$ :

$$\frac{d}{dt}W_t = \frac{i}{\hbar} [W_t, H + V_t] \quad . \quad (11.3)$$

$V_t$  is a possibly explicitly time dependent perturbation of the system. Before the perturbations has been switched on, the system was in an equilibrium state,

$$W_t \rightarrow G = e^{\beta(F - H)} \quad \text{for } t \rightarrow -\infty \quad . \quad (11.4)$$

Recall that  $F$  is the system's free energy which guarantees  $\text{tr}G = 1$ , and  $\beta = 1/k_B T$  where  $T$  is the temperature of the Gibbs state.

As explained in detail in section 4, (11.3) is best solved in the interaction picture, with states and observables time translated according to (11.2). One arrives at the following integral equation which combines the differential equation (11.3) and the initial condition (11.4):

$$W_t(t) = G + \int_{-\infty}^t ds \frac{i}{\hbar} [W_s(s), V_s(s)] \quad . \quad (11.5)$$

A sensible result: the state now, at time  $t$ , depends on previous states and on previous perturbations only, and on the initial state. Small perturbations will cause only small deviations from the initial state.

### 11.1 Higher order response

The zeroth order approximation is  $W_t(t) = G + \dots$ . The first order contribution is obtained by inserting the lowest order into (11.5):

$$\int_{-\infty}^t ds \frac{i}{\hbar} [G, V_s(s)] + \dots \quad . \quad (11.6)$$

The second order addition is

$$\int_{-\infty}^t ds \int_{-\infty}^s du \frac{i}{\hbar} \left[ \frac{i}{\hbar} [G, V_u(u)], V_s(s) \right] + \dots \quad . \quad (11.7)$$

The expectation value of an observable  $M$  is  $\text{tr} GM(t) = \text{tr} GM$  in lowest approximation. The next term (linear response) is

$$\int_{-\infty}^t ds \text{tr} G \frac{i}{\hbar} [V_s(s), M(t)] . \quad (11.8)$$

The quadratic response may be written as

$$\int_{-\infty}^t ds \int_{-\infty}^s du \text{tr} G \frac{i}{\hbar} [V_u(u), \frac{i}{\hbar} [V_s(s), M(t)]] . \quad (11.9)$$

Let us now specialize to

$$V_t = -\lambda(t)V . \quad (11.10)$$

The linear response contribution (11.8) is

$$\int_0^{\infty} d\tau_1 \lambda(t - \tau_1) \Gamma^{(1)}(\tau_1) \quad (11.11)$$

with

$$\Gamma^{(1)}(\tau_1) = \text{tr} G \frac{i}{\hbar} [M, V(-\tau_1)] . \quad (11.12)$$

(11.9) reads

$$\int_0^{\infty} d\tau_1 \int_0^{\infty} d\tau_2 \lambda(t - \tau_1) \lambda(t - \tau_1 - \tau_2) \Gamma^{(2)}(\tau_1, \tau_2) \quad (11.13)$$

with

$$\Gamma^{(2)}(\tau_1, \tau_2) = \text{tr} G \frac{i}{\hbar} [ \frac{i}{\hbar} [M, V(-\tau_1)], V(-\tau_1 - \tau_2) ] . \quad (11.14)$$

Note that also the second order response function  $\Gamma^{(2)}(\tau_1, \tau_2)$  is an expectation value in the unperturbed Gibbs state.

## 11.2 Susceptibilities

Let us Fourier transform  $m(t) = \text{tr} W_t M - \text{tr} GM$  and  $\lambda(t)$ . We arrive at the following expression,

$$\hat{m}(\omega) = \chi^{(1)}(\omega) \hat{\lambda}(\omega) + \int \frac{du}{2\pi} \chi^{(2)}(u, \omega - u) \hat{\lambda}(u) \hat{\lambda}(\omega - u) + \dots , \quad (11.15)$$

with

$$\chi^{(1)}(\omega_1) = \int_0^{\infty} d\tau_1 e^{i\omega_1 \tau_1} \Gamma^{(1)}(\tau_1) , \quad (11.16)$$

$$\chi^{(2)}(\omega_1, \omega_2) = \int_0^\infty d\tau_1 e^{i(\omega_1 + \omega_2)\tau_1} \int_0^\infty d\tau_2 e^{i\omega_2\tau_2} \Gamma^{(2)}(\tau_1, \tau_2) , \quad (11.17)$$

and so forth.

For the interaction of the electromagnetic field with matter, in electric dipole approximation, we replace (11.10) by

$$V_t = - \int d^3x E_i(t, \mathbf{x}) P_i(\mathbf{x}) . \quad (11.18)$$

$\mathbf{E}(t, \mathbf{x})$  is a time dependent external electric field,  $\mathbf{P}(\mathbf{x})$  the polarization at  $\mathbf{x}$ . As usual, we use the same symbol for the polarization (as an observable) and its expectation value. Its Fourier transform is

$$\hat{P}_i(\omega) = \chi^{(1)}(\omega) \hat{E}_j(\omega) + \int \frac{du}{2\pi} \chi_{ijk}^{(2)}(u, \omega - u) \hat{E}_j(u) \hat{E}_k(\omega - u) + \dots \quad (11.19)$$

The expression

$$\chi_{ij}^{(1)}(\omega_1) = \int_0^\infty d\tau_1 e^{i\omega_1\tau_1} \int d^3\xi \left\langle \frac{i}{\hbar} [P_i(0, 0), P_j(-\tau_1, \boldsymbol{\xi})] \right\rangle \quad (11.20)$$

for the linear response susceptibility has been thoroughly studied in previous sections.

The quadratic response is described by

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega_1, \omega_2) = & \\ & \int_0^\infty d\tau_1 e^{i(\omega_1 + \omega_2)\tau_1} \int_0^\infty d\tau_2 e^{i\omega_2\tau_2} \int d^3\xi \int d^3\eta \\ & \left\langle \frac{i}{\hbar} \left[ \frac{i}{\hbar} [P_i(0, 0), P_j(-\tau_1, \boldsymbol{\xi})], P_k(-\tau_1 - \tau_2, \boldsymbol{\eta}) \right] \right\rangle . \end{aligned} \quad (11.21)$$

(11.21) is already a rather complicated expression. What is the counterpart to the Kramers-Kronig relation? What is the counterpart to the fluctuation-dissipation theorem? Does the second law of thermodynamics hold up to second order response theory? Are there symmetries with respect to frequencies and tensorial indices? Non-linear response theory is not yet well investigated, and we shall stop at this point.

### 11.3 Second harmonic generation

$\chi_{ijk}^{(2)}(\omega_1, \omega_2)$  is a proper tensor of rank three, symmetric in the second and third index. It vanishes if the Gibbs state is invariant with respect to space inversion. Only crystals without inversion center will respond in second order to perturbations by an electric field<sup>14</sup>.

<sup>14</sup> $\chi_{ijk}^{(2)}(0, \omega)$  is the same as  $\chi_{ijk}^{20}(\omega)$  which describes the Pockels effect.

Let us discuss lithium niobate,  $\text{LiNbO}_3$ . We choose a coordinate system such that the  $z$ -axis coincides with the crystallographic  $c$ -axis. See appendix B for details. Assume a light wave traveling with wave number  $q$  in  $x$ -direction, being polarized in  $y$ -direction. The relation between angular frequency  $\omega$  and wave number is

$$q = n^o(\omega) \frac{\omega}{c} , \quad (11.22)$$

where  $n^o$  is the ordinary refractive index. The plane wave is described by

$$E_1 = E_3 = 0 \text{ and } E_2(t, \mathbf{x}) = A e^{-i\omega t} e^{iqx} . \quad (11.23)$$

$\chi_{122}^{(2)}$  and  $\chi_{222}^{(2)}$  vanish, therefore the second order polarization response is

$$P_1 = P_2 = 0 \text{ and } P_3(t, \mathbf{x}) = A^2 \chi_{322}^{(2)} e^{-2i\omega t} e^{2iqx} . \quad (11.24)$$

In general, this does not excite a light wave because frequency and wave number do not fit. Only if the phase matching condition

$$2q = n^e(2\omega) \frac{2\omega}{c} \quad (11.25)$$

holds, (11.24) will excite an electromagnetic plane wave. Note that it propagates with the extraordinary refractive index.

(11.22) and (11.25) amount to

$$n^o(\omega) = n^e(2\omega) . \quad (11.26)$$

The ordinary refractive index of lithium niobate is always larger than the extraordinary. Since both increase—in the infrared or visible—with frequency, condition (11.26) can be met, for a certain angular frequency  $\bar{\omega}$ . This frequency to be doubled depends on all quantities which affect the refractive indices, such as temperature, composition of the material etc.

Note that the intensity of frequency doubled light grows quadratically with the intensity of incident light. In particular, a resonator which confines  $\omega$ -light and is leaky for  $2\omega$ -light, allows high conversion rates.

Frequency doubling or tripling is technically important because cheap semiconductor lasers emit light of low frequency, while many optical applications demand short wavelengths.

Frequency doubling is well known in music. Musical instruments are highly non-linear. A harmonic tone (of one frequency only) always excites other tones, such as the octave, or the second harmonic. Therefore, frequency doubling is also known as second harmonic generation, or SHG.



## A Causal functions

Assume

$$f(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} g(\omega) \quad (\text{A.1})$$

where  $g = g(\omega)$  is analytic. It is a simple exercise to prove

$$f(t) = 0 \text{ for } t < 0 \quad (\text{A.2})$$

provided  $g = g(\omega)$  is holomorphic<sup>15</sup> in the upper plane  $\text{Im } \omega > 0$ . The converse is also true. If  $f = f(t)$  is a causal function, as characterized by (A.2), its Fourier transform  $g = g(\omega)$  is holomorphic in the upper half plane.

Hence,  $f(t) = \theta(t)f(t)$  holds true which may be expressed as

$$g(\omega) = \int \frac{du}{2\pi} \frac{g(u)}{\epsilon - i(\omega - u)} , \quad (\text{A.3})$$

where the limit  $0 < \epsilon \rightarrow 0$  is understood. The Fourier transform of a product is the convolution of the respective Fourier transforms.

(A.3) says that the pole at  $u = \omega$  has to be avoided in the lower plane. Adding and subtracting an integration path which avoids the singularity  $u = \omega$  in the upper half plane results in

$$g(\omega) = -i \text{Pr} \int \frac{du}{\pi} \frac{g(u)}{u - \omega} . \quad (\text{A.4})$$

$\text{Pr} \int$  denotes the principal value integral, the average of avoiding the singularity in the lower and the upper half plane. The dispersion relation

$$g'(\omega) = \text{Pr} \int \frac{du}{\pi} \frac{g''(u)}{u - \omega} \quad (\text{A.5})$$

is a simple consequence, where  $g'$  is the real and  $g''$  the imaginary part of  $g$ . The Fourier transform of a causal function obeys a Kramer-Kronig like dispersion relation.

So far we never required  $f = f(t)$  to be real. If  $f$  is a causal function, then  $if$  is causal as well. Therefore,

$$g''(\omega) = \text{Pr} \int \frac{du}{\pi} \frac{g'(u)}{\omega - u} \quad (\text{A.6})$$

is an alternative formulation.

If  $f$  is also real, then its Fourier transform must obey  $g^*(\omega) = g(-\omega)$ .  $g' = g'(\omega)$  is an even and  $g'' = g''(\omega)$  an odd function. This then implies

$$g'(\omega) = \text{Pr} \int_0^\infty \frac{du}{\pi} \frac{2u g''(u)}{u^2 - \omega^2} . \quad (\text{A.7})$$

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<sup>15</sup>analytic and free of singularities

Now, only positive frequencies need to be considered. The counterpart to (A.6) is

$$g''(\omega) = 2\omega \text{Pr} \int_0^\infty \frac{du}{\pi} \frac{g'(u)}{\omega^2 - u^2} . \quad (\text{A.8})$$

Let us study an example.  
The Fourier transform of

$$f(t) = \theta(t) e^{-\Gamma t} \quad (\text{A.9})$$

is

$$g(\omega) = \frac{1}{\Gamma - i\omega} . \quad (\text{A.10})$$

Indeed, this Fourier transform has a singularity at  $\omega = -i\Gamma$  in the lower half plane (we assume  $\Gamma > 0$ ), and it respects  $g(\omega) = -g^*(-\omega)$ . The real and imaginary parts read

$$g'(\omega) = \frac{\Gamma}{\Gamma^2 + \omega^2} , \quad g''(\omega) = \frac{\omega}{\Gamma^2 + \omega^2} , \quad (\text{A.11})$$

they are even and odd functions of  $\omega$ , respectively.

$$\text{Pr} \int \frac{du}{\pi} \frac{1}{u + i\Gamma} \frac{1}{u - \omega} = \frac{1}{\Gamma - i\omega} \quad (\text{A.12})$$

is easily established, and the real part and imaginary part of this identity are the dispersion relations (A.5) and (A.6).

By the way, (A.9) is the Green's function for a relaxation process.

$$\dot{p} + \Gamma p = F(t) \quad (\text{A.13})$$

is solved by

$$p(t) = \int_0^\infty d\tau e^{-\Gamma\tau} F(t - \tau) . \quad (\text{A.14})$$

## B Crystal symmetry

The electromagnetic interaction, which governs the field of solid state physics, is invariant with respect to translations in space and time, rotations, space inversion, time reversal, and boosts. Let us concentrate on a body at rest, hence the boosts need not be considered any more. We have already investigated the consequences of invariance with respect to time reversal, so let us disregard this aspect here as well. We remain with spatial translations, rotations, and inversion. We first discuss why a symmetric Hamiltonian may give rise to an unsymmetric equilibrium state. This phenomenon, the spontaneous breakdown of symmetry, is widespread, in particular, when a system is very large, like a carbon hydrogen molecule or an ideally infinite crystal.

### B.1 Spontaneous symmetry breaking

The Hamiltonian  $H$  of ordinary matter is invariant with respect to translation, rotation, and inversion. Consequently, the equilibrium, or Gibbs state, which is a function of the Hamiltonian, should also be invariant with respect to translations, rotations, and inversion. This is obviously wrong. Crystals have preferred directions (crystal axes), and they need not have an inversion center. In general, the symmetry of a theory does not imply the symmetry of the ground state of a particular system. Symmetry may be broken spontaneously. Just think about the planetary system. Although there is rotational invariance, the planets do not move on spheres (how should they?) or circles. Rotational symmetry merely says that a planetary system which is tilted by a certain angle would be possible as well.

However, quantum mechanics teaches something else. The hydrogen atom, for example, is not a minute planetary system. All possible electron orbits interfere in such a way that the ground state is truly spherically symmetric.

Another, less trivial example is the ground state of the ammonia molecule  $\text{NH}_3$ . The three protons form an equilateral triangle. The nitrogen ion is either above or below. In fact, the ground state is a symmetrical superposition of above/below, and its energy is lower, by a tiny amount, than the energy of the anti-symmetrical superposition. The energy difference  $\hbar\omega_0$  defines the microwave frequency standard ( $f_0 = 23.87012$  MHz).

The larger the molecule, the less probable is a transition between a state and its mirror-image. The right-handed version of a glucose molecule may, in principle, become a left handed version. The true ground state is a symmetric combination of both, but since so many nuclei would have to change position simultaneously, the transition time exceeds the age of the universe by orders of magnitude. Hence, if produced by a right handed plant, a dextrose molecule will stay in a state which defies the principle of inversion symmetry.

The same applies to crystals. For instance, if  $\text{LiNbO}_3$  is grown, an electric current defines a preferred direction. Once the crystal cools down, it keeps its  $c$ -axis orientation. Not even the largest external electric field may revert the crystal's polarization.

## B.2 Symmetry groups

One has to distinguish between translations and point transformations. A crystal lattice consists of translated copies of a unit cell. A point symmetry element sends each ion of the cell to another position such that the transformed cell looks the same. The point symmetry elements can be an inversion center, a mirror plane, a 1, 2, 3, 4, or 6-fold rotation axis, or a 1, 2, 3, 4, or 6-fold rotation axis with inversion. These point symmetry elements form groups, altogether 32, each describing a crystal symmetry class. There is an internationally accepted short hand notation system. For example,  $3m$  says that there is a three-fold rotation axis, without inversion, and a mirror plane such that the rotation axis lies in that plane.  $\bar{3}m$  would indicate an additional reflection symmetry with respect to a plane orthogonal to the rotation axis. Consult the standard work by Nye<sup>16</sup> for details.

## B.3 A case study

Let us discuss lithium niobate  $\text{LiNbO}_3$ , a non-centric crystal of class  $3m$ . This symmetry class allows proper tensors of rank 3.

The symmetry group consists of the identity  $I$ , a reflection

$$\Pi = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (\text{B.1})$$

and a  $120^\circ$  rotation

$$R = \begin{pmatrix} -\sqrt{1/4} & \sqrt{3/4} & 0 \\ -\sqrt{3/4} & -\sqrt{1/4} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (\text{B.2})$$

The entire group  $3m$  is made up of  $\{I, \Pi, R, R^{-1}, \Pi R, R\Pi\}$ , because of  $R^2 = R^{-1}$ ,  $\Pi^2 = I$  and  $\Pi R^{-1} = R\Pi$ . The multiplication table is

	$I$	$\Pi$	$R$	$R^{-1}$	$\Pi R$	$R\Pi$
$I$	$I$	$\Pi$	$R$	$R^{-1}$	$\Pi R$	$R\Pi$
$\Pi$	$\Pi$	$I$	$\Pi R$	$R\Pi$	$R$	$R^{-1}$
$R$	$R$	$R\Pi$	$R^{-1}$	$I$	$\Pi$	$\Pi R$
$R^{-1}$	$R^{-1}$	$\Pi R$	$I$	$R$	$R\Pi$	$\Pi$
$\Pi R$	$\Pi R$	$R^{-1}$	$R\Pi$	$\Pi$	$I$	$R$
$R\Pi$	$R\Pi$	$R$	$\Pi$	$\Pi R$	$R^{-1}$	$I$

(B.3)

<sup>16</sup>J. F. Nye, Physical Properties of Crystals, their Representation by Tensors and Matrices; Oxford University Press

We denote by  $\hat{c}$  the polar three-fold symmetry axis (a vector of unit length) and by  $\hat{u}$ ,  $\hat{v}$ ,  $\hat{w}$  three unit vectors in a plane orthogonal to it, with angles of  $120^\circ$  between them. We identify  $\hat{u} = \hat{x}$  and choose  $\hat{y}$  orthogonal to it. This means

$$\hat{v} = -\sqrt{\frac{1}{4}}\hat{x} + \sqrt{\frac{3}{4}}\hat{y} \quad \text{and} \quad \hat{w} = -\sqrt{\frac{1}{4}}\hat{x} - \sqrt{\frac{3}{4}}\hat{y} . \quad (\text{B.4})$$

$\hat{x} \rightarrow -\hat{x}$  should be a symmetry as well as a permutation of  $\hat{u}$ ,  $\hat{v}$ , and  $\hat{w}$ .  $\hat{c} \rightarrow -\hat{c}$  must not be a symmetry. After all, we deal with  $3m$ , not  $\bar{3}m$ . We look for a third rank tensor  $d_{ijk} = d_{ikj}$  which would describe the Pockels effect or second harmonic generation.

$$D_{ijk}^{(1)} = \hat{c}_i \hat{c}_j \hat{c}_k \quad (\text{B.5})$$

fulfills all requirements.

$\hat{u}_j \hat{u}_k + \hat{v}_j \hat{v}_k + \hat{w}_j \hat{w}_k$  is a symmetric second rank tensor with three-fold rotation symmetry. A short calculation shows that it is proportional to  $\hat{x}_i \hat{x}_j + \hat{y}_i \hat{y}_j$ . Consequently,

$$D_{ijk}^{(2)} = \hat{c}_i (\hat{x}_j \hat{x}_k + \hat{y}_j \hat{y}_k) \quad (\text{B.6})$$

is another admissible rank 3 tensor. A third possibility is

$$D_{ijk}^{(3)} = \hat{x}_i (\hat{c}_j \hat{x}_k + \hat{x}_j \hat{c}_k) + \hat{y}_i (\hat{c}_j \hat{y}_k + \hat{y}_j \hat{c}_k) . \quad (\text{B.7})$$

Another tensor, namely  $\hat{u}_i \hat{u}_j \hat{u}_k + \hat{v}_i \hat{v}_j \hat{v}_k + \hat{w}_i \hat{w}_j \hat{w}_k$ , proportional to

$$\hat{x}_i (\hat{x}_j \hat{x}_k - \hat{y}_j \hat{y}_k) - \hat{y}_i (\hat{x}_j \hat{y}_k + \hat{y}_j \hat{x}_k) , \quad (\text{B.8})$$

is not acceptable, because it is antisymmetric with respect to  $\hat{x} \rightarrow -\hat{x}$ . However, we only need to replace  $\hat{u}$  by  $\hat{c} \times \hat{u}$ , and the same for  $\hat{v}$  and  $\hat{w}$  which amounts to interchanging  $\hat{x}$  and  $\hat{y}$ . Instead of (B.8) we now obtain the fourth tensor

$$D_{ijk}^{(4)} = \hat{y}_i (\hat{y}_j \hat{y}_k - \hat{x}_j \hat{x}_k) - \hat{x}_i (\hat{x}_j \hat{y}_k + \hat{y}_j \hat{x}_k) . \quad (\text{B.9})$$

Not that the first three tensors are invariant with respect to  $\hat{x} \leftrightarrow \hat{y}$ , so  $\hat{c} \times \hat{u}$  instead of  $\hat{u}$  etc. does not produce new tensors. For the point group  $3m$  there are just four linearly independent tensors of rank 3.

The most general rank 3 tensor with  $3m$  symmetry may be written as

$$d_{ijk} = \sum_{r=1}^4 d_r D_{ijk}^{(r)} \quad (\text{B.10})$$

with four different invariants  $d_r$  which depend on the effect and the material under study.

We list the non-vanishing tensor elements:

$$d_1 = d_{333} , \tag{B.11}$$

$$d_2 = d_{311} = d_{322} , \tag{B.12}$$

$$d_3 = d_{131} = d_{113} = d_{223} = d_{232} , \tag{B.13}$$

$$d_4 = d_{222} = -d_{211} = -d_{112} = -d_{121} . \tag{B.14}$$

A word of caution. Some authors represent a symmetric matrix by a six component vector:

$$T_{ij} = \begin{pmatrix} T_1 & T_6 & T_5 \\ T_6 & T_2 & T_4 \\ T_5 & T_4 & T_3 \end{pmatrix} . \tag{B.15}$$

When summing over indices, they count the off-diagonal index pairs, such as  $6 = (1, 2) = (2, 1)$ , only once. Consequently you will find factors 2 in some such tables. The rank 3 tensor  $d_{ijk}$  is represented by a  $3 \times 6$  matrix  $d_{i\ell}$  where  $i$  runs from 1 to 3 and  $\ell$  from 1 to 6. In our case, (B.14) might read  $d_{16} = -2d_{22}$ . Nye<sup>17</sup> follows this convention.

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<sup>17</sup>Physical properties of Crystals, loc. cit.

## C Glossary

**Birefringence** In the absence of *gyrotropy* the refractive part of the *susceptibility* tensor  $\chi_{ij}$ , and with it the permittivity tensor  $\epsilon_{ij} = \delta_{ij} + \chi_{ij}$  are real and symmetric. There is a Cartesian coordinate system such that the permittivity is diagonal,  $\epsilon_{ij} = \epsilon^{(i)} \delta_{ij}$ . A plane wave, linearly polarized along the  $i^{\text{th}}$  coordinate axis, propagates with main *refractive index*  $n = \sqrt{\epsilon^{(i)}}$ . If all three eigenvalues of the permittivity tensor coincide, the medium is optically isotropic. If two are equal and differ from the third, there is a preferred axis. Light propagating along this optical axis may be polarized arbitrarily, but perpendicular to the optical axis. The corresponding main refractive index is called ordinary. Light propagating perpendicular to the optical axis is characterized by the main extraordinary refractive index. Crystals with an optical axis, or uniaxial crystals, are birefringent. If all three eigenvalues of the permittivity tensor differ, one speaks of a biaxial crystal.

**Cotton-Mouton effect** A quasi-static external magnetic field, or the saturation magnetization of a ferro- resp. ferri-magnetic crystal, also contributes in second order to the susceptibility (Cotton-Mouton effect). The susceptibility change  $\Delta\chi_{ij}^{\text{cm}} = \chi_{ijkl}^{02} M_k M_l$  is not bound to special crystal properties,  $\chi_{ijkl}^{02} \propto \delta_{ij} \delta_{kl}$  is allowed. Because it is quadratic in the magnetization, the Cotton-Mouton effect is reciprocal, in contrast to the *Faraday effect*.

**Dissipation-fluctuation theorem** If a system is disturbed by a time dependent addition  $-\lambda(t)V$  to the Hamiltonian, the absorption of energy is described by the imaginary part of the corresponding susceptibility. Fluctuations of the equilibrium state are measured by the spectral density. Both functions, the dissipative part of the susceptibility and the spectral density, are intimately related, because of the *Kubo-Martin-Schwinger identity*. In particular, the *Wiener-Khintchin theorem* allows the proof of a weak form of the second law of thermodynamics.

**Faraday effect** An external quasi-static magnetic field  $\mathbf{B}$  causes a change of the susceptibility by  $\Delta\chi_{ij}^{\text{fe}} = i\epsilon_{ijk} g_k$ , where the gyration vector  $\mathbf{g}$  (see *gyrotropy*) depends linearly on the magnetic field strength, or the saturation magnetization. If linearly polarized light passes a medium with Faraday effect, its polarization vector is rotated by an angle  $\Theta L$ , where  $L$  is the path length within the medium and  $\Theta$  the specific Faraday rotation constant. If the light beam is reflected and passes the medium a second time, but backward, the polarization vector is rotated by the same amount, such that both angles add. This property allows to build an *optical isolator*.

**Gibbs state** The equilibrium states of matter  $G(T, \lambda) \propto \exp -H(\lambda)/k_B T$ , or Gibbs states, depend on temperature  $T$  and on external parameters  $\lambda$  appearing in the Hamiltonian  $H$ . Besides chemical composition these may be mechanical

stress, an external electric field, or an external magnetic field. If the external parameters or the temperature of the system's environment change slowly enough, then  $W_t \approx G(T_t, \lambda_t)$  is a good approximation. The state  $W_t$  is always very close to an equilibrium state, and we speak of a reversible process. If the external parameters vary rapidly, the system is always away from equilibrium, and we speak of an irreversible process.

**Gyrotropy** A gyrotropic contribution to the susceptibility is formally described by  $\Delta\chi_{ij}^{\text{gy}} = i\epsilon_{ijk}g_k$ .  $\mathbf{g}$  is the gyrotropy vector. If light propagates in the direction of  $\mathbf{g}$ , the eigenmodes are circularly polarized waves with different refractive indices. When a linearly polarized wave enters a gyroscopic medium, it is split into circularly polarized waves which propagate with different phase velocities. If this beam leaves the medium, the circularly polarized waves are recombined into a linearly polarized wave. The polarization vector of this outgoing wave is rotated by an angle  $\Theta L$ , where  $L$  is the path length within the gyroscopic medium. Note that the sign of rotation, right (clockwise) or left (anti-clockwise), is judged by an observer facing the light source. *Optical activity* and the *Faraday effect* cause gyrotropy.

**Hall effect** If charged particles within a solid move in a static magnetic field, the current contains a component which is proportional to the driving electric field, proportional to the quasi-static induction field, and perpendicular to both. These properties are a consequence of *Onsager's theorem* for kinetic coefficients, such as the tensor of electric conductivity. The sign of the Hall constant depends on whether electrons or electron wholes dominate the charge transport mechanism.

**Interaction picture** The state  $W$  is defined by preparing the system under study in a well-described manner. An observable  $M$  is a class of equivalent measuring procedures which, for all states, show the same results. Both are represented, in conventional quantum theory, by self-adjoint linear operators mapping a Hilbert space into itself. Time enters the game as follows. After preparing the state  $W$  and before measuring  $M$ , one may wait for a time  $t$ . This either defines a state  $W_t$  (Schrödinger picture) or an observable  $M_t$  (Heisenberg picture). Waiting is described by the unitary waiting operator  $U_t = \exp(-itH/\hbar)$ , an exponential function of time  $t$  and an observable  $H$ , the energy, or Hamiltonian.

The interaction picture is in-between. Often the Hamiltonian is the sum of a manageable part  $H$  and a perturbation  $V$ . It is advisable to resort to the Heisenberg picture with  $H$ . Then the Schrödinger equation for states is driven by  $V$  only, giving rise to a power series expansion in  $V$ .

**Kerr effect** The second order electro-optic Kerr effect  $\Delta\chi_{ij}^{\text{ke}} = \chi_{ijkl}^{20} E_k E_l$  is allowed even for otherwise isotropic media. It is usually much weaker than the *Pockels effect*, if present.



**Kramers-Kronig relation** The Hermitian part  $\chi'_{ij}$  of the susceptibility tensor describes refraction, the anti-Hermitian contribution  $i\chi''_{ij}$  absorption. The refractive part at a certain angular frequency  $\omega$  is an integral over all frequencies  $u$  of the absorptive part, weighted by  $1/(\omega - u)$ . There is no refraction without absorption, although possibly in another frequency domain. And: refractive indices depend necessarily on angular frequency. The Kramers-Kronig relation is a consequence retarded *response functions*.

**Kubo-Martin-Schwinger identity** Formally, the *Gibbs* state is equivalent to the time translation operator with the inverse temperature as an imaginary time. This results in  $\langle BA(z) \rangle = \langle A(z - i\hbar\beta)B \rangle$  for an arbitrary imaginary time  $z$ .  $A$  and  $B$  are observables,  $A(t)$  is the time-translated observable, and  $A(z)$  a proper analytic continuation. The KMS identity is an important step in deriving the *dissipation-fluctuation theorem*.

**Linear response** A system, originally in an equilibrium, or *Gibbs* state, may be perturbed by an explicitly time-dependent addition  $-\lambda(t)V$  to the otherwise constant Hamiltonian  $H$ . The equation of motion and the initial condition may be formulated as an integral equation which can be expanded into a power series in  $\lambda$ . The first non-trivial contribution describes the response of the system to such perturbations which is linear in the driving force  $\lambda = \lambda(t)$ . By construction, the linear response, as described by *response functions*, is retarded.

**Onsager relations** A symmetry relation for the generalized susceptibility tensor based on the invariance of physical laws with respect to time reversal. The susceptibility tensor is symmetric provided the direction of an external magnetic field is reversed. It can be extended to the tensor of kinetic coefficients describing the linear relationship between generalized fluxes and driving forces. Onsager relations are relevant for the tensorial properties of various effects, such as *birefringence*, the *Pockels effect*, *Kerr effect*, *Faraday effect*, *Cotton-Mouton effect*, *optical activity*, and the *Hall effect*.

**Optical activity** The susceptibility depends on angular frequency and on the wave vector,  $\chi_{ij} = \chi_{ij}(\omega, \mathbf{q})$ . The dependence on  $\mathbf{q}$  is weak, and  $\chi_{ij}(\omega)$  suffices for most applications. In some cases, however, the first order of an expansion in  $\mathbf{q}$  will result in an detectable effect, namely in a rotation of the polarization vector along the propagation path. This gyrotropic effect is known as optical activity. It will occur only if the material is left-right hand asymmetric, such as quartz or a solution of dextrose.

**Optical axis** A direction such that a beam propagating along it has a *refractive index* which does not depend on polarization. For optically isotropic media, any direction is an optical axis. If two eigenvalues of the permittivity tensor coincide, but differ from the third, there is but one optical axis. If all three eigenvalues are different, one has two optical axes.

**Optical isolator** A bulk optical isolator consists of a polarizer, a crystal with Faraday effect rotating the polarization by  $45^\circ$ , and another polarizer being rotated by  $45^\circ$  with respect to the first. If light which has passed the isolator is reflected and possibly de-polarized, the polarization of the reflected wave passing the second polarizer is rotated by another  $45^\circ$ ; it is therefore blocked by the first polarizer. Optical isolators are required to protect a laser from its own light. An integrated optical isolator is the goal of intensive research effort.

**Pockels effect** A linear opto-electric effect  $\Delta\chi_{ij}^{\text{pe}} = \chi_{ijk}^{10} E_k$  is possible for ferro-electric or piezo-electric crystals which possess no inversion symmetry center. This Pockels effect allows to switch or modulate light beams. It is usually much stronger than the Kerr effect.

**Refractive index** Plane harmonic waves are characterized by an angular frequency  $\omega$  and a wave vector  $\mathbf{q}$ . With  $\mathbf{w}$  (a unit vector) as the direction of propagation and  $k_0 = \omega/c$  one may write  $\mathbf{q} = n k_0 \mathbf{w}$ . This defines the refractive index  $n$  of the wave. If the *susceptibility*, consequently the permittivity tensor  $\epsilon_{ij} = \delta_{ij} + \chi_{ij}$  is real and symmetric (no absorption, no *gyrotropy*), one may choose a Cartesian coordinate system such that  $\epsilon$  becomes diagonal. The square roots of the diagonal entries (eigenvalues) are sometimes called main refractive indices. They are refractive indices if the wave is polarized along the corresponding main axis.

**Response function** If  $H_t = H - \lambda(t)V$  drives a process, than the expectation value of an observable  $M$  at time  $t$  is the equilibrium expectation value plus a retarded integral over the driving force  $\lambda = \lambda(t)$ . The Green's, or response function  $\Gamma(\tau)$  is proportional to the equilibrium expectation value of the commutator  $[M(\tau), V]$ . The Fourier transform over positive ages  $\tau$  is a *susceptibility*.

**Second harmonic generation** The quadratic response of a medium to perturbations of angular frequency  $\omega$  produces a polarization of double frequency. Only crystals without inversion center show this effect, such as lithium niobate. Efficient frequency doubling requires phase matching.

**Susceptibility** If the Gibbs, or equilibrium state is disturbed by a time dependent addition  $-\lambda(t)V$  to the Hamiltonian, the expectation values of observables  $M$  vary with time, at lowest order with the same frequency as the perturbation. The Fourier transform of  $\langle M \rangle_t - \langle M \rangle$  is linearly related with the Fourier transform  $\hat{\lambda}$ , the susceptibility  $\chi = \chi(\omega)$  being the constant of proportionality. Susceptibilities are Fourier transforms of corresponding *response functions*  $\Gamma(\tau)$  over positive ages  $\tau$ .

**Wiener-Khintchin theorem** The process  $t \rightarrow M(t)$  in a stationary state is described by the time auto-correlation function  $K(\tau)$  indicating how much

$M(\tau)$  is still correlated with  $M(0)$ . The Fourier transform of  $K(\tau)$ , the spectral density  $S(\omega)$ , is never negative. A very short correlation time results in an almost constant spectral density which qualifies the process  $t \rightarrow M(t)$  as white noise. The Wiener-Khintchin and the *dissipation fluctuation theorem* allow to prove the second law of thermodynamics.