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THEORY OF ENERGY TRANSFER PROCESSES IN SOLIDS: MODES, COHERENT– AND NON–MARKOVIAN PROPERTIES

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ABSTRACT

An introduction to the description of energy transfer processes in condensed matter is given with special emphasis on the definition of the energy– and energy–current–density, relevant modes, coherent/incoherent and Markovian/non–Markovian dynamics.

1. Introduction

According to our present understanding of nature the notion of energy forms the basis of physics[1] as well as other natural sciences, industry, economy, and society.[2] Quoting Freeman J. Dyson:[3]

> *“Even within the framework of physical science energy has a transcendent quality. On many occasions when revolutions in thought have demolished old sciences and created new ones, the concept of energy has proved to be more valid and durable than the definitions in which it was embodied”.*

The central role of energy originates – apart from its conservation – that its change is accomplished with the change of at least one further extensive quantity, e.g. linear and angular momentum $(\mathbf{p}, \mathbf{L})$, position $(\mathbf{r})$, charge (Q), vector potential $(\mathcal{A})$, polarization $(\mathcal{P})$, magnetization $(\mathcal{M})$, Entropy (S), Volume (V), or particle number N, etc.[4]

$$dE = \mathbf{v}d\mathbf{p} - \mathbf{F}d\mathbf{r} + \Omega d\mathbf{L} + \Phi dQ + \mathbf{j}d\mathcal{A} + \mathcal{E}d\mathcal{P} + \mathcal{H}d\mathcal{M} + TdS - pdV + \mu dN \ldots, \quad (1)$$

Table. 1. Examples of energy transfer.

system	modes of energy transport	examples
vacuum	electromagnetic radiation	solar energy flux
	kinetic energy of massive particles	particle reactions
	internal (or chemical) energy	excited atoms
gases	flow, convection	atmosphere
	density waves	sound waves
	type–II collisions between atoms	He–Ne laser pump
fluids	heat flow	house heating system
	particle flow	hydraulic system
	flow of chemical energy	oil pipe line
	convection, diffusion,...	
solids	charge transport	electric power lines
	localized states	photosynthesis
	collective excitations	phonons, excitons...

where the intensive variables $\mathbf{v}$ (velocity), $\mathbf{F}$ (force), etc. have their usual meaning.* With exception of $\mathbf{r}$ and V, all other extensive variables have a density and a current and, thus, they play a different role: $\mathbf{r}$ labels different spatially separated subsystems of size V which are described by densities of energy, momentum, etc. In a perceptive view $\mathbf{p}$, $\mathbf{L}$, Q, ... play the part of "energy-carriers".

A review on energy transfer processes up to 1983 can be found in the Proceedings of a previous summer institute on the same topic[5] whereas this volume[6] documents the progress obtained. Since 1969 the INSPEC database provides more than 53000 entries on energy transfer processes, yet only about 1100 papers are related to coherence and 130 study (non-) Markovian properties. The latter subjects are of interest in the excitonic energy transport in molecular crystals[7] and, in particular, for the description of ultrafast processes in optically excited semiconductors.[8] The scope of this article is to give an introduction of the description of the conservation and flow of energy (Chapter 2.), construction of energy density and energy current density of the systems of interest, and examples of (normal-) modes (Chapter 3.), description of (ir–)reversible and (in-)coherent dynamics (Chapter 4.), and (non-)Markovian (memory function) properties (Chapter 5.). Various examples will be given or can be found in this volume.[6]

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[*] Notation: Vectors and tensors in boldface, the magnitude of a vector $\mathbf{v}$ is denoted by the same letter, e.g. $v = |\mathbf{v}|$. Matrices and operators are set with a hat, e.g. $\widehat{a}$. Electromagnetic fields are set in calligraphic style, e.g. $\mathcal{E}, \mathcal{B}$.

2. Conservation and Flow of Energy

Quoting Richard P. Feynman[9]

> *"If a cat were to disappear in Pasadena and at the same time appear in Erice, that would be an example of the global conservation of cats. This is not the way cats are conserved. Cats or charge or baryons are conserved in a much more continuous way. If any of these quantities begin to disappear in a region, they begin to appear in a neighbouring region. Consequently, we can identify a flow of charge out of a region with disappearance of charge inside a region. This identification of divergence of a flux with the time rate of change of a charge density is called a local conservation law. A local conservation law implies that the total charge is conserved globally, but the reverse does not hold. However, relativistically it is clear that non-local global conservation laws cannot exist, since to a moving observer the cat will appear in Erice before it disappears in Pasadena.*

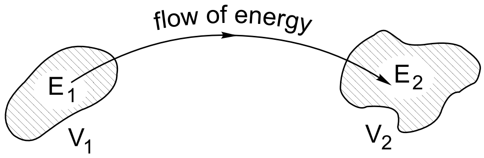


Figure 1: Schematic of the flow of energy through the surface of a volume.

If there is a change of energy in a certain portion of space it may either flow across the surface of V or it is exchanged with another system which is not explicitely considered here, see Fig.1. Like cats the rate of change of an extensive variable G [†] is governed by a relation of the form

$$\frac{dG}{dt} = -J_G + \Sigma_G \,, \tag{2}$$

where $\frac{dG}{dt}$ and Σ_G (=production rate of G) depends on the volume V of the portion of space and J_G (=current) depends on the surface of V.

For a conserved quantity, such as electrical charge or energy $\Sigma_G = 0$ whereas for entropy $\Sigma_S \geq 0$. Sometimes, however, merely the energy balance of a subsystem is considered, e.g. the electromagnetic field may gain or loose energy by interaction with the mechanical system of the charges so that $\Sigma_E \neq 0$ if Σ_E refers to the electromagnetic field alone.

As the size and shape of the volume V considered in Eq. (2) is arbitrary, a local formulation of a conservation law can be derived by using Gauss' law

$$\frac{\rho_G(\mathbf{r},t)}{\partial t} + \mathrm{div}\ \mathbf{j}_G(\mathbf{r},t) = \sigma_G(\mathbf{r},t)\,. \tag{3}$$

[†] G denotes the name as well as the quantity.

$\rho_G(\mathbf{r},t), j_G(\mathbf{r},t)$ and $\sigma_G(\mathbf{r},t)$ respectively denote the density, current density, and production rate density of G. In addition, the relations of these quantities to the state variables have to be specified.

It is an old question whether an energy current can be imagined as energy moving with a well–defined velocity[10] yet a solution has been worked out only recently for some cases.[11] In a kinematic interpretation, one assumes a decomposition of the form $j_E = \rho_E \mathbf{v}_E$, like it is known to hold for the particle current of a one–component fluid, $\mathbf{j}_N = \rho_N \mathbf{v}_N$, where, ρ_N, $\mathbf{v}_N$ are state variables of the fluid which can be measured independently. In particular, $\mathbf{v}_N$ is the velocity of a reference frame in which $\mathbf{j}_N$ is locally zero. For several components the current density consists of several terms

$$\rho_N = \sum_i \rho_i, \quad \mathbf{j}_N = \sum_i \rho_i \mathbf{v}_i \, , \tag{4}$$

where i labels different particle numbers N_i. Note, $j_N = \rho_N \mathbf{v}_N$ may appear as self–evident, –nevertheless, it does not define a particle transport velocity $\mathbf{v}_N$ which, in general, can be measured independently and, hence, such a velocity is of no physical relevance. This holds for the energy–current velocity, too. The situation is even more queer for the momentum balance of the electromagnetic field. For a pure electrostatic field the momentum density ($=\mathcal{E} \times \mathcal{H}/c$) is zero everywhere, whereas, the momentum–current denstity (= negative Maxwellian stress tensor) has nonzero (diagonal) components, see Landau–Lifshitz[14] (Vols. 2,8). In some special cases, however, $\mathbf{v}_E = \mathbf{j}_E/\rho_E$ is identical with the group velocity of a wave puls. Furthermore, a decomposition of the form of Eq.(4) may sometimes be appropriate in terms of plane-wave modes of the system which play the part of particle numbers degree of freedom.

3. Density, Current, and Modes of Energy Transfer

In this chapter, we will construct and list of results for the energy density, energy current density and (normal–) modes of basic systems and equations which are frequently used to describe energy transfer processes. Normal modes of a system are defined as particular solutions of the respective (homogeneous, linear) field equations supplemented by appropriate boundary conditions. (In some cases, such modes could even be chosen as complex functions even though the physical fields are real.) Their importance and utility lies in the fact, that arbitrary field configurations can be expanded in terms of these modes which themselves represent a type of stationary states. In Quantum Mechanics these modes are the eigenstates of the Hamiltonian. The following chapter gives some selected examples. For a discussion of nonlinear waves see, e.g. the review article by Bishop et al.[12]

3.1. Scalar Waves

Propagation of scalar (complex) waves are described by the wave–equation

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)\Psi(\mathbf{r},t) = s(\mathbf{r},t)\,, \tag{5}$$

where $s(\mathbf{r},t)$ describes an external source. The state of a wave-field is fixed by $\Psi(\mathbf{r},t_0) = \Phi(\mathbf{r})$ and $\dot{\Psi}(\mathbf{r},t_0) = \Theta(\mathbf{r})$, where $\Phi(\mathbf{r}), \Theta(\mathbf{r})$ are two arbitrary functions. The homogeneous part of Eq. (5) is (form-) invariant under time reversal and, thus, describes reversible processes. By standard manipulations the energy density, current- and production rate densities can be found

$$\begin{aligned}
\rho_E(\mathbf{r},t) &= \frac{1}{2}\frac{\rho_m}{c^2}\left|\frac{\partial\Psi(\mathbf{r},t)}{\partial t}\right|^2 + \frac{1}{2}\rho_m\left|\text{grad }\Psi(\mathbf{r},t)\right|^2\,, && (6)\\
\mathbf{j}_E(\mathbf{r},t) &= -\rho_m\Re\left(\frac{\partial\Psi^*(\mathbf{r},t)}{\partial t}\text{grad }\Psi(\mathbf{r},t)\right)\,, && (7)\\
\sigma_E(\mathbf{r},t) &= \rho_m\Re\left(\frac{\partial\Psi^*(\mathbf{r},t)}{\partial t}s(\mathbf{r},t)\right)\,, && (8)
\end{aligned}$$

where ρ_m denotes the mass-density (or another appropriate quantity) and $\Re$ means real part, see e.g. the textbook by Barton.[13]

Expressions of this form are relevant to all scalar waves, though the physical significance of the individual terms may be different. For example, for an elastic continuum Ψ denotes the displacement of a volume element, $c = \sqrt{E/\rho_m}$ is the velocity of sound, and E is the bulk modulus, see Landau-Lifshitz[14] (Vol.7). For a nonviscous compressible fluid, on the other hand, Ψ is the velocity potential, $\mathbf{v} = -\text{grad}\psi$ and Eqs.(6-7) can be rewritten as

$$\rho_E(\mathbf{r},t) = \frac{1}{2}\rho_m v^2 + \rho_m\epsilon\,, \qquad \mathbf{j}_E(\mathbf{r},t) = \left(\frac{1}{2}\rho_m v^2 + \rho_m w\right)\mathbf{v}\,. \tag{9}$$

Here the energy density is just the sum of the kinetic and internal energy ϵ (per unit mass), $w = \epsilon + p/\rho_m$ is the enthalpy (per unit mass), and p is the pressure, see Landau-Lifshitz[14] (Vol. 6). $\mathbf{j}_E$ consists of two terms: the term $\rho_E\mathbf{v}$ represents the energy which is "transmitted convectively" whereas the term $p\mathbf{v}$ is traditionally described as "the work per sectional area" which is done by the fluid.[11]

Next we consider the modes of the (homogeneous) wave–equation Eq. (5) ($s = 0$) by separation of the variables $\mathbf{r}, t$

$$\Psi_\kappa(\mathbf{r},t) = e^{-i\omega_\kappa t}\Psi_\kappa(\mathbf{r})\,. \tag{10}$$

κ labels different mode functions which obey the (homogeneous) Helmholtz-equation

$$\left[\Delta + \left(\frac{\omega_\kappa}{c}\right)^2\right]\Psi_\kappa(\mathbf{r}) = 0\,. \tag{11}$$

An arbitrary solution of the (homogeneous) wave–equation can be decomposed in modes

$$\Psi(\mathbf{r},t) = \sum_{\kappa} \left[A_{\kappa}^{(+)} e^{-i\omega_{\kappa} t} + A_{\kappa}^{(-)} e^{+i\omega_{\kappa} t}\right] \Psi_{\kappa}(\mathbf{r})\,, \tag{12}$$

where the two independent functions $A_{\kappa}^{(\pm)}$ are fixed by the initial conditions. For real fields, these functions are not independent.

The simplest modes are plane waves, $\Psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})$, where $\kappa = \mathbf{k}$ is the wave vector and $\omega_{\mathbf{k}} = ck$. Remarkably, the energy current of such a mode is just energy density $\rho_E(\mathbf{r},t) = \rho_m k^2$ times c, $\mathbf{j}_E(\mathbf{r},t) = \rho_E(\mathbf{r},t) c\hat{\mathbf{k}}$ (see end of Chapter 2.).

As an example, we consider the propagation of (longitudinal) waves in one-dimension (no source term), where the general solution can be explicitely stated in terms of two arbitrary functions $f^{(\pm)}(x)$, which are fixed by the initial conditions.

$$\Psi(x,t) = f^{(+)}(x-ct) + f^{(-)}(x-ct)\,. \tag{13}$$

Individually, $f^{(\pm)}(x)$ describe wave–packets which are propagating in ±x directions. Tab. 2. summarizes the results for two special cases.

Table 2. Solutions of the one–dimensional wave equation (D'Alembert–solution). Left: Displacement–, right: momentum–excitation at $t = 0$.

	$\Psi(x,0) = \Phi(x), \quad \dot{\Psi}(x,0) = 0$	$\Psi(x,0) = 0, \quad \dot{\Psi}(x,0) = \Theta(x)$
$\Psi(x,t)$	$\frac{1}{2}\left[\Phi(x-ct) + \Phi(x+ct)\right]$	$\frac{1}{2c}\int_{x-ct}^{x+ct} \Theta(x')dx'$
$\rho_E(x,t)$	$\frac{\rho_m}{4}\left[\Phi'^2(x-ct) + \Phi'^2(x+ct)\right]$	$\frac{\rho_m}{4c^2}\left[\Theta^2(x-ct) + \Theta^2(x+ct)\right]$
$j_E(x,t)$	$\frac{\rho_m}{4}\left[\Phi'^2(x-ct) - \Phi'^2(x+ct)\right] c$	$\frac{\rho_m}{4c^2}\left[\Theta^2(x-ct) - \Theta^2(x+ct)\right] c$

(14)

The prime denotes differentiation with respect to the argument. These solutions explicitely show that the energy current can be decomposed into two parts of opposite directions, each moving with velocity c,[11] see Fig.2. The mean square displacement with respect to $\rho_E(x,t)$ is $< x^2 > (t) = (ct)^2$.

Finally, we notice a property of wave propagation in two dimensions which is in strange contradiction with our daily experience. In three-dimensions, an initial pulse of finite duration propagating off the source will always create a wave packet with a leading as well as a trailing edge. In two dimensions, however, there is no trailing edge and, hence, an observer will find an infinite afterglow, see Fig. 3. Remarkably, this property holds in all space dimensions of even order $d = 2, 4, 6$ etc.

For spherical or cylindrical waves and solutions of the inhomogeneous wave equation in terms of Green-functions, see e.g. Barton's book.[13]

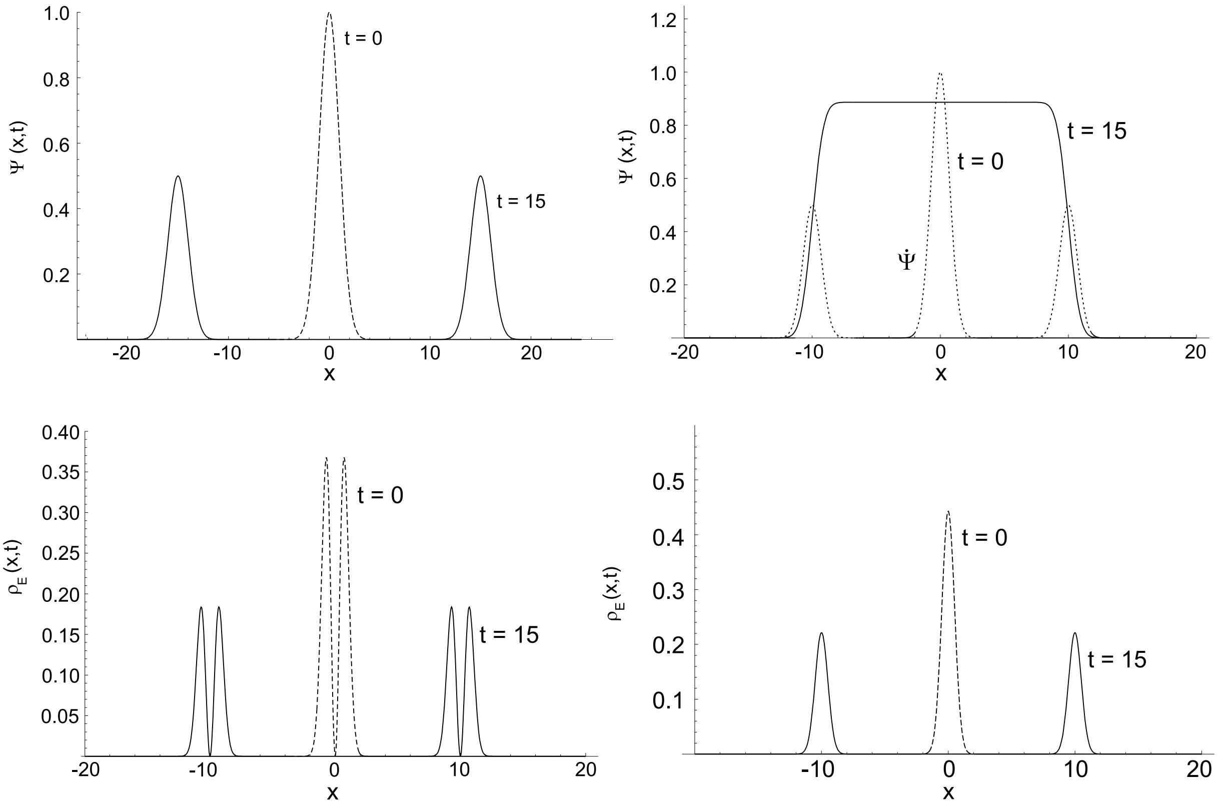


Figure 2: Time evolution of an initial wave–packet and its energy–density. Initial conditions: $\Psi(x, 0) = \Phi(x)$ (left) and $\Psi(x, 0) = \Theta(x)$ (right). $\Phi(x), \Theta(x)$ are Gaussians centered at $x = 0$. Note, the dotted curves in right upper graph display the velocity. (Dimensionless quantities.)

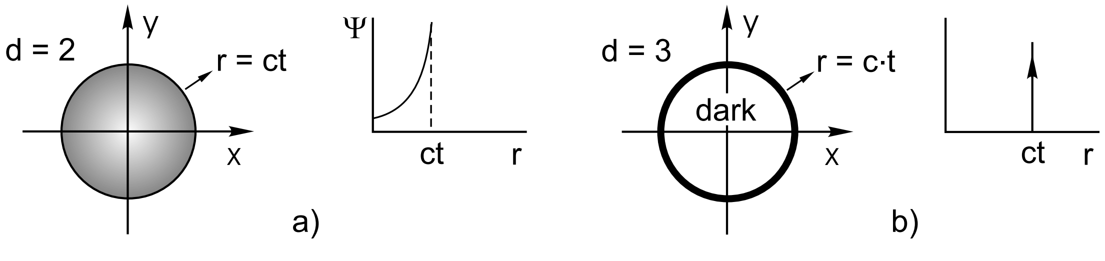


Figure 3: Pulse propagation in d=2 dimensions shows an infinite afterglow whereas pulses in d=3 dimensions display a leading as well as a trailing edge.

3.2. Diffusion

Consider a conserved quantity with density ρ with a diffusive flow, $j = -D\text{grad}\rho$ (=Fick's law) where D is the diffusion constant. By construction, ρ obeys the diffusion equation $\frac{\partial\rho}{\partial t} = D\Delta\rho$. For notational convenience, we shall write Ψ (which is assumed to be real) instead of ρ, where Ψ may describe the density of particles, charge, energy, etc., and allow for an external source term $s(\mathbf{r}, t)$.

$$\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} - D\Delta\Psi(\mathbf{r}, t) = s(\mathbf{r}, t)\,. \tag{15}$$

The state of this system is fixed by $\Psi(\mathbf{r}, 0) = \Phi(\mathbf{r})$. In contrast to the wave–equation, Eq. (15) is not symmetric with respect to time–reversal and, thus, describes irreversible processes.

The modes of the (homogeneous) diffusion equation ($s = 0$) are defined as

$$\Psi_\kappa(\mathbf{r}, t) = e^{-\lambda_\kappa t}\Psi_\kappa(\mathbf{r})\,. \tag{16}$$

κ labels different mode–functions which are again solutions of the (homogeneous) Helmholtz-Eq. (11) where $(\omega_\kappa/c)^2$ has to be replaced by λ_κ/D. An arbitrary solution of Eq.(15) (with $s(\mathbf{r}, t) = 0$) can be decomposed as

$$\Psi(\mathbf{r}, t) = \sum_\kappa A_\kappa e^{-\lambda_\kappa t}\Psi_\kappa(\mathbf{r})\,, \tag{17}$$

where the real coefficients A_κ are determined by the initial condition.

A very useful solution of Eq.(15) is the "heat pole" which belongs to $\Psi(\mathbf{r}, 0) = \delta(\mathbf{r})$, see Fig.4.

$$\Psi(\mathbf{r}, t) = (4\pi Dt)^{-\frac{d}{2}} e^{-\frac{r^2}{4Dt}}\,, \quad t > 0\,, \tag{18}$$

where $d = 1, 2, 3$ is the space dimension. The mean square displacement with respect to Eq.(18) is $< x^2 > (t) = 2Dt$. Remarkably, this result holds in any dimension if x refers to one of the components of the d–dimensional position vector. The solution

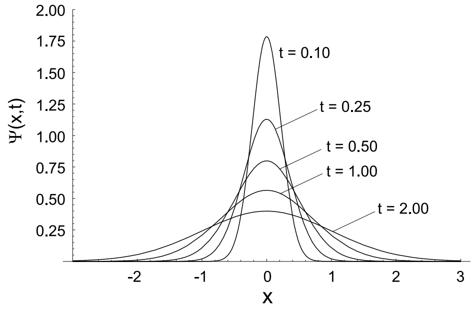


Figure 4: Time evolution of the "heat pole".

Eq.(18) is also called the propagator and denoted by $K(\mathbf{r},t)$ as it propagates the initial state to finite times

$$\Psi(\mathbf{r},t) = \hat{U}_D(t)\Psi(\mathbf{r},0) = \int K(\mathbf{r}-\mathbf{r}',t)\Psi(\mathbf{r}',0)d^d\mathbf{r}' \,. \tag{19}$$

3.3. Electromagnetic Field

The state of the electromagnetic field (EMF) in a vacuum is described by two vector fields $\mathcal{E},\mathcal{B}$ whose time-evolution is determined by the Maxwell-equations, see Landau–Lifshitz[14] (Vol. 8)

$$\begin{array}{rclrcl} \dfrac{\partial\mathcal{E}}{\partial t} - c^2\text{curl }\mathcal{B}\,, & = & -\dfrac{1}{\epsilon_0}\mathbf{j}(\mathbf{r},t), & \text{div }\mathcal{E} & = & \dfrac{1}{\epsilon_0}\rho(\mathbf{r},t), \\ \dfrac{\partial\mathcal{B}}{\partial t} + \text{curl }\mathcal{E} & = & 0\,, & \text{div }\mathcal{B} & = & 0\,. \end{array} \tag{20}$$

The two equations containing the divergences represent "auxilary conditions" (as $\rho(\mathbf{r},t)$ is assumed to be prescribed) rather than dynamic equations. $c = 1/\sqrt{\epsilon_0\mu_0}$ is the speed of light and $\rho,\mathbf{j}$ denote the electrical charge density and current density, respectively. The Maxwell–equations are (form-) invariant under time reversal $t \to -t$, $\mathbf{j} \to -\mathbf{j}$, $\rho \to \rho$, $\mathcal{E} \to \mathcal{E}$, $\mathcal{B} \to -\mathcal{B}$ and, therefore, describe reversible processes.

By standard manipulations of Eqs. (20) a conservation law is derived

$$\frac{\partial}{\partial t}\left(\frac{\epsilon_0}{2}\mathcal{E}^2 + \frac{1}{2\mu_0}\mathcal{B}^2\right) + \text{div }\left(\mathcal{E}\times\frac{\mathcal{B}}{\mu_0}\right) = -\mathbf{j}\mathcal{E}\,, \tag{21}$$

which describes the energy–balance of the EMF. Thus, by comparison with Eq.(3)

$$\rho_E(\mathbf{r},t) = \frac{\epsilon_0}{2}\mathcal{E}^2 + \frac{1}{2\mu_0}\mathcal{B}^2\,, \quad \mathbf{j}_E(\mathbf{r},t) = \mathcal{E}\times\frac{\mathcal{B}}{\mu_0}\,, \quad \sigma_E(\mathbf{r},t) = -\mathbf{j}\,\mathcal{E}\,. \tag{22}$$

Traditionally, $\mathbf{j}_E(\mathbf{r},t)$ is called the Poynting-vector and $\sigma_E(\mathbf{r},t)$ is interpreted as the work done by the EMF on the charges.

A variety of different modes of the EMF is known which are used for the description of fields in free space and for microwave– or laser–resonators. In infinite space the simplest modes are transverse, linear polarized, travelling plane–waves

$$\mathcal{E}(\mathbf{r},t) = \mathcal{E}_0\cos(\mathbf{kr}-\omega t), \qquad \mathcal{B}(\mathbf{r},t) = \frac{1}{c}\hat{\mathbf{k}}\times\mathcal{E}(\mathbf{r},t)\,, \tag{23}$$

where $\hat{\mathbf{k}}$ is a unit vector along the wave vector $\mathbf{k}$, $\mathbf{k}\cdot\mathcal{E}_0 = 0$, and $\omega = ck$. The energy density and energy current density of this mode are

$$\rho_E(\mathbf{r},t) = \epsilon_0\mathcal{E}_0^2\cos^2(\mathbf{kr}-\omega t), \quad \mathbf{j}_E(\mathbf{r},t) = \rho_E(\mathbf{r},t)\,c\,\hat{\mathbf{k}}\,. \tag{24}$$

Note, for this mode the energy current density is particularily simple: it is just energy density times the velocity of light.

In many cases the flow of energy occurs along rather unexpected paths so that the Poynting-form of the energy current density has been frequently questioned. In particular, the nonzero energy flow in (crossed) static and magnetic fields appears to be "unphysical" and other forms of $\mathbf{j}_E$ (which still are in accordance with Eq. (21)) have been proposed.[15] Nevertheless, there are convincing arguments that the Poynting form of the energy current (which is also the momentum density times c) is correct, see Vol. II, 17-5, 27-4, and 27-11 of the Feynman–lectures.[16]

3.4. Electromagnetic Field in Matter

According to the atomic structure of matter the microscopic fields are spatially strongly fluctuating on an atomic scale. Instead of the true microscopic fields, averaged (macroscopic) fields are used, which are likewise denoted by $\mathcal{E}, \mathcal{B}$, see Landau–Lifshitz[14] (Vol. 8).

$$\begin{aligned} \frac{\partial \mathcal{D}(\mathbf{r},t)}{\partial t} - \mathrm{curl}\, \mathcal{H}(\mathbf{r},t) &= -\mathbf{j}(\mathbf{r},t), & \mathrm{div}\ \mathcal{D}(\mathbf{r},t) &= \rho(\mathbf{r},t), \\ \frac{\partial \mathcal{B}(\mathbf{r},t)}{\partial t} + \mathrm{curl}\ \mathcal{E}(\mathbf{r},t) &= 0\,, & \mathrm{div}\ \mathcal{B}(\mathbf{r},t) &= 0\,. \end{aligned} \tag{25}$$

The averaged total charge– and current– densities in matter are separated in three groups:

- those who are counted explicitely as $\rho, \mathbf{j}$,
- "displacement charges/currents" $\rho_d = -\mathrm{div}\ \mathcal{P}$, $\mathbf{j}_d = \dot{\mathcal{P}}$, and
- "magnetization currents" $\mathbf{j}_m = \mathrm{curl}\ \mathcal{M}$, ($\rho_m = 0$ as div $\mathbf{j}_m = 0$).

The polarization $\mathcal{P}$ and magnitization $\mathcal{M}$ fields combine with $\mathcal{E}$, $\mathcal{B}$ to two new fields $\mathcal{D} = \epsilon_0 \mathcal{E} + \mathcal{P}$ and $\mathcal{H} = \mathcal{B}/\mu_0 - \mathcal{M}$. For a tutorial on the dielectric descriptions of semiconductors see, e.g., Ref.[27]

By standard manipulations of Eqs.(25) a conservation law is derived

$$\frac{\partial}{\partial t}\left(\frac{\epsilon_0}{2}\mathcal{E}^2 + \frac{\mu_0}{2}\mathcal{H}^2\right) + \mathrm{div}\ (\mathcal{E}\times\mathcal{H}) = -\mathbf{j}\mathcal{E} - \mathcal{E}\frac{\partial \mathcal{P}}{\partial t} - \mu_0 \mathcal{H}\frac{\partial \mathcal{M}}{\partial t}\,, \tag{26}$$

which is identified with the conservation of energy. Note, the appearance of $\mathcal{H}$, whereas the averaged microscopic magnetic field is $\mathcal{B}$! Note also, that the rhs of Eq. (26) may contain dissipative as well as non-dissipative parts. Some parts of the latter can be combined with $\mathcal{E}\times\mathcal{H}$ to form an energy–current vector of the combined system EMF + matter.[17]

For nondispersive, nonconducting matter, $\mathcal{P} = \epsilon_0(\epsilon - 1)\mathcal{E}$, $\mathcal{M} = (\mu - 1)\mathcal{H}, \mathbf{j} = 0$, where ϵ, μ are assumed to be constant. In this case, we may define an energy balance of the combined system EMF + Matter (denoted by a tilde) by

$$\tilde{\rho}_E = \frac{1}{2}\mathcal{E}\mathcal{D} + \frac{1}{2}\mathcal{B}\mathcal{H}\,, \quad \tilde{\mathbf{j}}_E = \mathcal{E} \times \mathcal{H}\,, \quad \tilde{\sigma}_E = 0\,, \tag{27}$$

where $\mathcal{D} = \epsilon_0\epsilon\mathcal{E}$ and $\mathcal{B} = \mu_0\mu\mathcal{H}$. For example, for a plane monochromatic wave, Eq.(23),

$$\tilde{\rho}_E(\mathbf{r}, t) = \epsilon_0\epsilon\mathcal{E}^2(\mathbf{r}, t)\,, \quad \mathbf{j}_E(\mathbf{r}, t) = \tilde{\rho}_E(\mathbf{r}, t)\frac{c}{n}\hat{\mathbf{k}}\,, \tag{28}$$

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

If dispersion is present, the situation is different. As an example, we consider uncoupled isotropically and harmonically bound charges $-e$ with density n and displacement s.[18] Omitting spatial dispersion, the polarization $\mathcal{P} = -nes$ obeys

$$\left(\frac{\partial^2}{\partial t^2} + \gamma\frac{\partial}{\partial t} + \omega_0^2\right)\mathcal{P}(\mathbf{r}, t) = \frac{ne^2}{m}\mathcal{E}(\mathbf{r}, t)\,. \tag{29}$$

When multiplying Eq.(29) by $\mathcal{P}$ we recover Eq. (26) which may be rewritten in the form of Eq.(3) with

$$\begin{aligned} \tilde{\rho}_E &= \frac{\epsilon_0}{2}\mathcal{E}^2 + \frac{\mu_0}{2}\mathcal{H}^2 + \frac{m}{ne^2}\left[\frac{1}{2}\left(\frac{\partial\mathcal{P}}{\partial t}\right)^2 + \frac{\omega_0^2}{2}\mathcal{P}^2\right]\,, && (30)\\ \tilde{\mathbf{j}}_E &= \mathcal{E} \times \mathcal{H}\,, && (31)\\ \tilde{\sigma}_E &= -\gamma\frac{m}{ne^2}\left(\frac{\partial\mathcal{P}}{\partial t}\right)^2\,. && (32) \end{aligned}$$

$\mathcal{H} = \mathcal{B}/\mu_0$. For a harmonic field as given by Eq.(23) the polarization is

$$\mathcal{P}(t) = \Re\left[\epsilon_0\chi(\omega)\mathcal{E}_0 e^{-i\omega t}\right]\,, \tag{33}$$

where $\chi(\omega) = \epsilon(\omega) - 1$ denotes the electrical susceptibility

$$\chi(\omega) = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}\,, \tag{34}$$

and $\omega_p^2 = (ne^2/m\epsilon_0)$ is the square of the plasma frequency, see Fig.5.

The time averaged energy– and current density of the combined EMF and matter are

$$\bar{\rho}_E = \frac{\epsilon_0}{4}\mathcal{E}_0^2\left[1 + |\epsilon(\omega)| + \frac{\omega_0^2 + \omega^2}{\omega_p^2}|\chi(\omega)|^2\right]\,, \quad \bar{j}_E = \frac{\epsilon_0}{2}\,\mathcal{E}_0^2\,n(\omega)c\,. \tag{35}$$

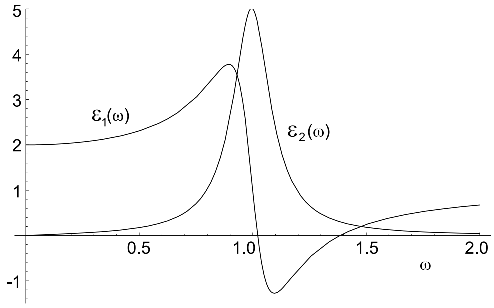


Figure 5: Dielectric function for harmonically bound charges.

$n = \Re\sqrt{\epsilon}$ is the real part of the refractive index. Outside the stop–band where $n(\omega) \neq 0$, and in the limit of zero damping, Eq.(35) can be rewritten as

$$\bar{\rho}_E = \frac{\epsilon_0}{2}\mathcal{E}_0^2 n(\omega)\frac{d[n(\omega)\omega]}{d\omega}\,. \tag{36}$$

Note, Eq.(36) is not a general result, in particular, it does not hold for finite damping, or in the region of anomalous dispersion.

3.5. Energy Transport Velocity and "Superluminal" Pulses

Presently there is a remarkable interest concerning the velocity of energy transport and the interpretation of "superluminal" pulses in dispersive media and wave guides, see e.g. a special issue of the "Annalen der Physik".[20] Although such phenomena are not new a great fuss arose. In particular, it was well known that the propagation of a puls with a Gaussian envelop[23–25] is essentially different compared to a semi–infinite envelop, which was initially studied by Sommerfeld and Brillouin.[21]

Pulse propagation experiments usually measure the cross-correlation function between the pulse travelled through matter along distance L and a reference pulse, see Fig.6. From that a delay/advance distance $\Delta s = c\Delta t$ a pulse velocity in matter $v_p = c/(1 + \Delta s/L)$ is deduced. It is well known that the group velocity

$$v_{gr}(k) = \frac{d\omega(k)}{dk} = c\left[\frac{d[n(\omega)\omega]}{d\omega}\right]^{-1} = \frac{c}{n(\omega) + \omega n'(\omega)}\,, \tag{37}$$

describes the propagation in a linear dispersive, nonabsorbing medium outside the stop band, where $\omega(k) = ck/n$. (If the refractive index is complex, one extrapolates Eq.(37) replacing $n(\omega)$ by its real part.) In the region of normal dispersion ($n'(\omega) > 0$) the group velocity is always smaller than c. However, in regions of strong anomalous dispersion ($n'(\omega) < 0$), v_{gr} can exceed c or even become negative. The common belief is that the meaning of Eq.(37) breaks down and the behaviour of the pulse becomes much more complicated. This is indeed true for the semi-infinite sinussoidal puls,[22] for

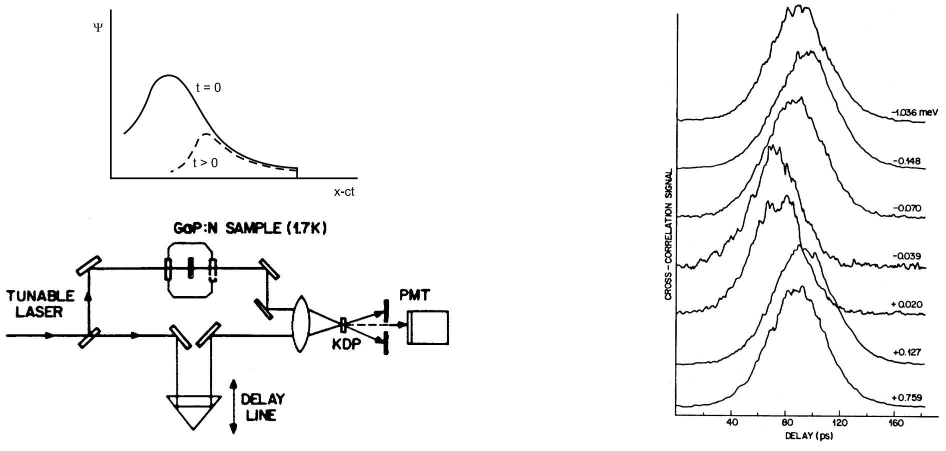


Figure 6: Left: Schematic of a Gaussian pulse propagating in a dispersive medium and of the experimental arrangement to measure the cross–correlation function. Right: a sample of the cross–correlation data as the laser is tuned through the exciton line of the $GaAs : N$ sample, $N = 1.5 \times 10^{17}\mathrm{cm}^{-3}$. According to Chu and Wong.[23]

a Gaussian shaped pulse, however, the situation is different. As discussed by Garrett and McCumber,[24] and in more detail by Oughstun and Balictsis,[25] the leading edge of the pulse is less attenuated than the trailing edge so that the pulse maximum speeds-up at the expense of the pulse height, see Fig.6. For a Fourier transform limited puls whose spectral width is much less than the width of the absorption line, the pulse propagates with the group velocity as given by Eq.(37) and even the shape and width of the pulse can remain almost intact after it emerges from the sample. Moreover, for undamped, harmonically bound electrons with a single resonance frequency the group velocity is identical with j_E/ρ_E; compare Eq.(36) with Eq.(37). The physics of puls propagation in wave guides below the cut–off frequency is similar, yet the pulse reshaping and attenuation is due to reflection rather than by absorption.[19] The propagation of an electron wave-packet through a potential barrier was studied by Krenzlin et al., see Ref.[20] (p. 732). Note, there is no indication of advance propagation of the leading pulse wing which, trivially, can never be surpassed. In addition, the time separation of two pulses is not affected so that there is no superluminal transmission of information, even if $v_{gr} > c$.

If a physically motivated definition of an energy transport velocity is desired, it ought to be based on a (local) Lorentz-transformation to a moving frame (denoted by a prime) of vanishing energy current

$$\mathcal{E} \to \mathcal{E}' = \gamma\left(\mathcal{E} + V \times \mathcal{B}\right), \tag{38}$$

$$\mathcal{B} \to \mathcal{B}' = \gamma\left(\mathcal{B} - \frac{V}{c^2} \times \mathcal{E}\right), \tag{39}$$

where $\gamma^{-2} = 1 - (V/c)^2$. Equating $\mathcal{E}' \times \mathcal{B}' = 0$, we obtain in the limit $V \ll c$

$$V = \frac{1}{2}\frac{j_E}{\rho_E} = \frac{\mathcal{E} \times \mathcal{B}}{\epsilon_0 \mu_0 \mathcal{E}^2 + \mathcal{B}^2} \, . \tag{40}$$

Remarkably, this velocity is numerically only, but one half of the “self evident” form.

3.6. Quantum Mechanics

In quantum physics, expressions for particle probability density and its current–density are well known from text books, yet expressions for energy–density and energy–current–density are less familiar. To construct these quantities, we first consider a single particle in one dimension in a time–dependent potential $V(x,t)$. The wave function $\psi(x,t)$ obeys the Schrödinger–equation

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \widehat{H}\psi(x,t)\, , \quad \widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t). \tag{41}$$

Under a time–reversal operation $\hat{T}\psi = \psi^*$, so that all expectation values remain unchanged. Hence, Eq. (41) describes reversible processes, see Landau–Lifshitz[14] (Vol.3, §7).

First, we find the energy–density starting from the expectation value of the Hamiltonian $\widehat{H}$

$$< \widehat{H} >= \int \psi^*(x,t)\widehat{H}\psi(x,t)\, dx = \int \rho_E(x,t)\, dx \, . \tag{42}$$

By partial integration we rewrite the integrand such that it is intrinsically positive, hence

$$\rho_E(x,t) = \frac{\hbar^2}{2m}\left|\frac{\partial \psi(x,t)}{\partial x}\right|^2 + V(x,t)\left|\psi(x,t)\right|^2 \, . \tag{43}$$

Next, we study the variation of $< \widehat{H} >$ with respect to time. Elimination of $\dot{\psi}$ by Eq.(41) and performing a partial integration we obtain for the integrand of $\frac{d}{dt} < \widehat{H} >$

$$\begin{aligned} I = i\frac{\hbar^3}{4m^2}\left\{\frac{\partial \psi^*}{\partial x}\frac{\partial^3 \psi}{\partial x^3} - \text{cc}\right\} - i\frac{\hbar}{2m}\left\{\frac{\partial \psi^*}{\partial x}\frac{\partial}{\partial x}\left[V(x,t)\psi(x,t)\right] - \text{cc}\right\} \\ + i\frac{\hbar}{2m}V(x,t)\left\{\psi^*\frac{\partial^2 t}{\partial x^2} - \text{cc}\right\} + \frac{\partial V(x,t)}{\partial \psi(x,t)}\left|\psi(x,t)\right|^2 \, . \end{aligned} \tag{44}$$

Now, the task is to rewrite the integral over I to extract the current–density via $-\frac{\partial}{\partial x}j_E(x) + \sigma_E(x,t)$. For the first term of Eq.(44) we get

$$-i\frac{\hbar^3}{4m^2}\frac{\partial}{\partial x}\left\{\frac{\partial \psi^*}{\partial x}\frac{\partial^2 \psi}{\partial x^2} - \text{cc}\right\} \, . \tag{45}$$

By partial integration, we find that the second term compensates the third one. Finally, the desired results for the energy–current and energy–production rate densities are

$$\begin{aligned} j_E(x,t) &= \Im\left\{\frac{\hbar^3}{2m}\frac{\partial\psi^*}{\partial x}\frac{\partial^2\psi}{\partial x^2}\right\} , \\ &= -\frac{\hbar^2}{m}\Re\left\{\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial t}\right\} + \frac{\hbar}{m}V(x,t)\Im\left\{\frac{\partial\psi^*}{\partial x}\psi(x,t)\right\} , \qquad (46) \\ \sigma_E(x,t) &= \frac{\partial V(x,t)}{\partial t}\left|\psi(x,t)\right|^2 . \qquad (47) \end{aligned}$$

For time–independent potentials, $\sigma_E(x,t) = 0$, as the energy is conserved. The generalization to three–dimensions is obvious by replacing $\frac{\partial}{\partial x}$ by grad .

As an example, we consider a free particle in a plane wave state $\psi(x,t) = \frac{1}{V_0}\exp(i\mathbf{kr})$, where V_0 is the normalization volume.

$$\rho_E(\mathbf{r},t) = \frac{E(\mathbf{k})}{V_0} , \quad \mathbf{j}_E(\mathbf{r},t) = \rho_E(\mathbf{r},t)\frac{\hbar\mathbf{k}}{m} , \qquad (48)$$

where $E(\mathbf{k}) = \hbar^2\mathbf{k}^2/2m$ is the energy of the particle.

The Schrödinger–equation of a free particle bears some analogy to the (homogeneous) diffusion–equation in “imaginary time”, $t_D \to it_S$. Eq.(17) can be viewed as the result of the application of the time–evolution operator $\widehat{U}_D(t)$ on the initial state

$$\Psi(\mathbf{r},t) = \widehat{U}_D(t)\Psi(\mathbf{r},0) , \quad \widehat{U}_D(t) = e^{-\widehat{H}t} , \qquad (49)$$

where $\widehat{H} = -D\Delta$ is the “Hamiltonian”. However, there is a profound difference between the diffusion equation and the Schrödinger–equation. Eq.(41) describes reversible processes and the solution can also be propagated backwards in time whereas it cannot for the (irreversible) diffusion–equation, because there are arbitrary large positive eigenvalues λ_k. In mathematical terms, the Schrödinger time evolution operator, $\widehat{U}_S(t) = \exp(-it\widehat{H}/\hbar)$, generates a group of unitary transformations, whereas $\widehat{U}_D(t)$, Eq.(19) is not unitary and generates only a semigroup which has no inverse element.

3.7. Collective Excitations in Solids

Condensed matter is a strongly interacting many body system which, in chemical terms, forms macromolecules with unsaturated bonds which allows for unlimited aggregation of particles. Due to the strong interaction between the (bare) particles (electrons, nuclei) no exact treatment is possible. However, in many cases a number of relevant features of the ground state as well as for the low–lying excitations have been recognized. For a review on basic notions in solid state physics see Anderson's book.[29] For our purposes, the most important properties are:

Ground state properties:

- broken symmetry: crystal, ferromagnet, superconductor…
- rigidity: mechanical, magnetic, gauge …

Low energy excitations:

- behave like a gas of weakly interacting (quasi-) particles,
- single particle excitations resemble the bare particles, at least at not too strong interactions (=adiabaticity),
- collective excitations are dynamically equivalent to the creation/absorption of bosons.

Broken symmetry means that the ground state of the system has a lower symmetry than the Hamiltonian. For example, the Hamilton of a solid is invariant under translations and rotations whereas the crystal state is not. (This is different for few–body systems, e.g. the hydrogen atom where the ground state has the full symmetry of the Hamiltonian.)

Rigidity refers to external perturbations. For example, condensed matter (fluids, solids) is almost incompressible, in addition, solids are rigid with respect to shear deformations. As an example of gauge-rigidity we consider the London-equations of a (type I) superconductor

$$\frac{\partial}{\partial t}\mathbf{j}(r,t) = \frac{ne^2}{m}\mathcal{E}(\mathbf{r},t)\,, \quad \mathrm{curl}\,\mathbf{j}(\mathbf{r},t) = -\frac{ne^2}{m}\mathcal{B}(\mathbf{r},t)\,, \tag{50}$$

where n is the density, m the mass, and $-e$ the charge of the electrons. Remarkably, these equations remain unchanged when replacing the electrons by Cooper–pairs with density $n/2$, charge $-2e$, and mass $2m$. We compare Eqs. (50) with the quantum mechanical result for the particle current of an electron in a magnetic field of vector potential $\mathcal{A}$, $\mathcal{B} = \mathrm{curl}\,\mathcal{A}$:

$$\mathbf{j}_N(\mathbf{r},t) = \frac{\hbar}{2mi}\left(\Psi^\dagger \mathrm{grad}\,\Psi - cc\right) - \frac{-e}{m}\left|\Psi(\mathbf{r},t)\right|^2 \mathcal{A}(\mathbf{r},t)\,. \tag{51}$$

For N particles, $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N)$ summation and integration of Eq.(51)on $N-1$ coordinates has to be included. If the many electron wave function is not affected by the magnetic field Eq.(51) (times $-e$) reduces to just the second London–equation (in the Coulomb–gauge, div $\mathcal{A} = 0$).

The concept of quasi–particles was originally developed by Landau who realized that there is a continuous mapping of the low energy excitation spectrum with the strength of the interparticle interactions, see Landau-Lifshitz,[14] (Vol. 5). Amazingly, this description holds even in relatively strong interacting systems like in metals or in liquid helium ^3He, ^4He. As an example of single–particle excitations we consider the transformation of free electrons to Bloch electrons in crystals, see Fig.7. In terms of quasi–particles, the excited states are described by occupation numbers $n_\alpha = 0, 1, 2...$, where α labels the one–particle states (or "modes") with energy ϵ_α. Hence, the excitation energy of the total system becomes

$$E(\{n_\alpha\}) - E_0 = \sum_\alpha \epsilon_\alpha n_\alpha + E_{int} \,. \tag{52}$$

E_0 is the ground state energy and $E_{int}(\{n_\alpha\})$ contains nonlinear terms in n_α which describe interactions between quasi–particles. For a translationally invariant system or a crystal, α is identical with the wave number $\mathbf{k}$, in addition, there may be several branches of wave-like excitations which will be labelled by an additional index ($= \nu$).

Collective modes are equivalent to a set of (uncoupled) harmonic oscillators with frequencies ω_α. Quantization of these oscillators directly leads to Eq.(52) which is dynamically equivalent to a system of bosons with energies $\hbar\omega_\alpha$, see Fig.8. In contrast to massive bosons, however, (e.g. He–atoms in liquid Helium) these quasi–particles can be easily created and destructed. An appropriate description of such processes is not possible within the "ordinary" wave–function formulation of quantum mechanics, and "second quantization"[‡] is needed.[30]

In the extended zone scheme quasi–momentum $\hbar\mathbf{k}$ plays almost the same role as real momentum. The two most important properties of particles and quasi–particles are

- The transport velocity of energy and momentum is given by

$$\mathbf{v}_T = \frac{\partial \epsilon(\mathbf{p})}{\partial \mathbf{p}}. \tag{53}$$

- The overall (quasi–) momentum and energy of particles and quasi–particles is conserved, see Fig.9.

Unfortunately, there is no general rule under which conditions such a scenario exists, and how to find the collective variables. Some examples will be given in the next sections. A survey on the dynamics and spectroscopy of collective excitations in solids,[32] and a collection of common and different properties of particles and quasi–particles[28] can be found in the Proceedings of two previous Erice–Schools.

[‡] The name "second quantization" is misleading. Besides $\hbar$ no second quantum constant arises. A better name is "occupation number representation", yet it is used in a different sense as position or momentum representation.

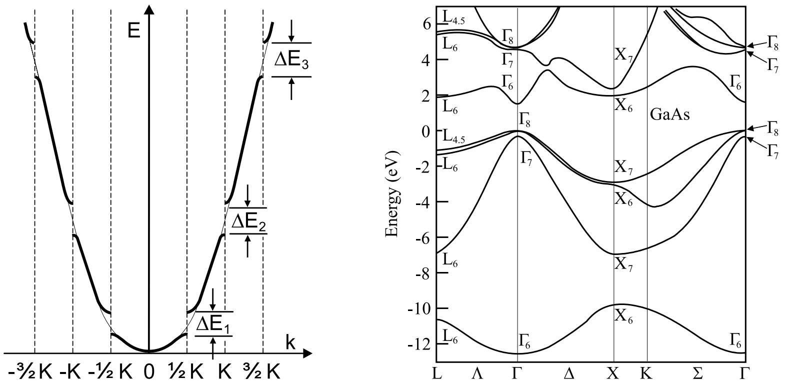


Figure 7: Left: Energy (quasi–)momentum relation of free electrons in an empty lattice (thin line) and in a weak periodic potential (solid line), where $K = 2\pi n/a$, $n = 0, \pm 1, \pm 2 \ldots$ are reciprocal lattice vectors. Right: Energy bandstructure of *GaAs* (in the reduced zone scheme). According to Cohen and Chelikowski.[31]

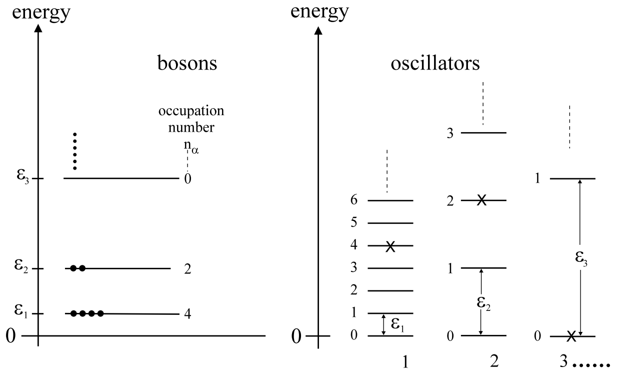


Figure 8: Equivalence of a system of N (noninteracting) bosons with single–particle energies ϵ_α and occupation numbers n_α and an infinite (uncoupled) set of harmonic oscillators with frequencies $\omega_\alpha = \epsilon_\alpha/\hbar$. Note that the zero–point energies of the oscillators are omitted. Dots symbolize particles, crosses excited states, respectively. $N = 6$. According to Ref.[28]

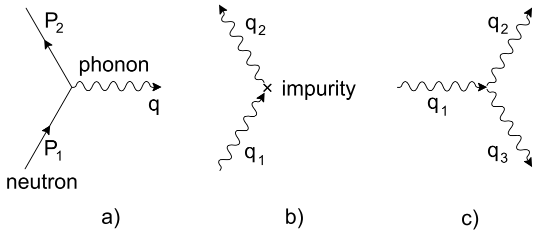


Figure 9: Examples of interactions between particles and quasi–particles. (a) Excitation of a phonon by neutron scattering, (b) scattering of a phonon by impurities, and (b) decay of a phonon due to anharmonic interactions. Energy and momentum are conserved at each particle/quasi–particle vertex whereas the impurity takes momentum but no energy.

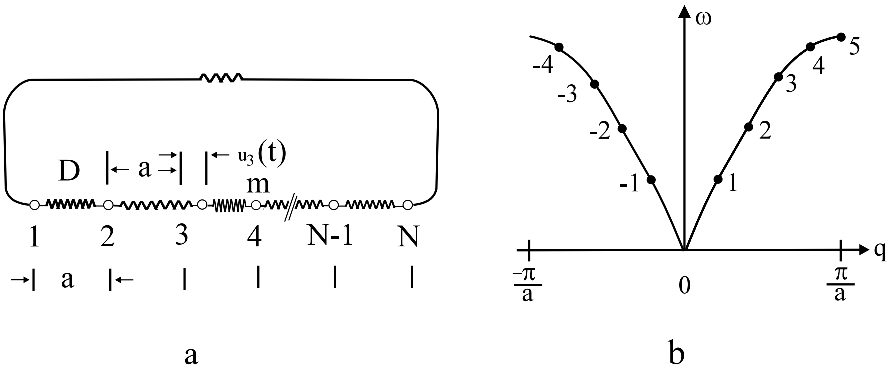


Figure 10: (a) Linear monoatomic chain with equal masses m and nearest neighbour springs D and periodic boundary conditions, (b) frequency spectrum for $N = 10$ "atoms". Note, there is no vibrational $q = 0$ mode (at $\omega = 0$); this degree of freedom is taken over by the common translational motion. According to Ref.[28]

A. Phonons

Phonons are quantized vibrations of a crystal–lattice. For notational simplicity, we consider first a linear chain of equal masses m and nearest neighbour springs, see Fig.10. Starting from the Hamiltonian in terms of canonical momenta p_j and displacements u_j of the masses at sites $j = 1, \ldots N$, $\{p_j, u_{j'}\} = \delta_{jj'}$

$$H = \sum_{j=1}^{N} \frac{1}{2m} p_j^2 + \frac{1}{2} D (u_{j+1} - u_j)^2 \,, \tag{54}$$

we first find the collective momenta P_k and coordinates Q_k

$$u_j = \sum_k \eta_j(k) Q_k \,, \quad p_j = \sum_k \eta_j^*(k) P_k \,, \quad \eta_j(k) = N^{-1/2} e^{ikja} \,. \tag{55}$$

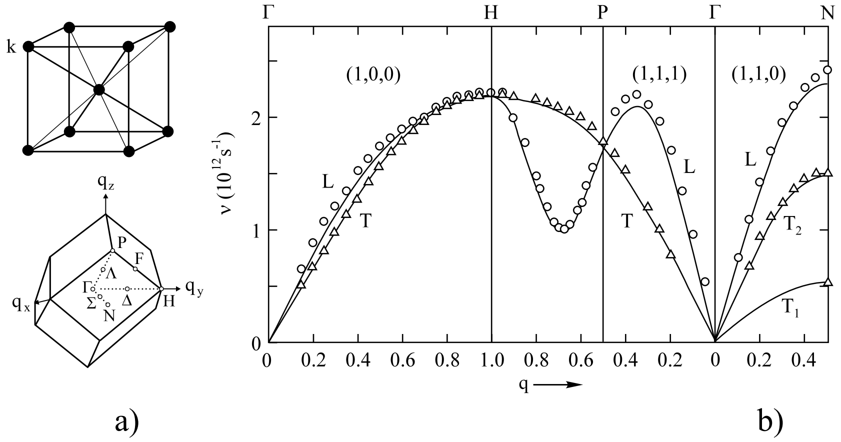
$\{a, b\}$ denotes the Poisson–bracket symbol, $k = \frac{2\pi}{Na}\kappa$, $\kappa = 0, \pm 1, \pm 2 ... \pm N/2$ is the wave–vector which is restricted to the first Brillouin–zone, and a is the lattice constant. Eq. (55) is canonical, $\{P_k, Q_{k'}\} = \delta_{kk'}$ and transforms Eq. (54) to a set of uncoupled oscillators with frequencies ω_k

$$H(P, Q) = \sum_k \frac{1}{2} P_k P_k^* + \frac{\omega_k^2}{2} Q_k Q_k^* \,, \quad \omega_k = \sqrt{\frac{4D}{m}} \sin \left| \frac{ka}{2} \right| \,. \tag{56}$$

In d dimensions, a vibrating lattice has d acoustic ($\omega_k = c_s |k|$ for $k \to 0$) and $d(s-1)$ optical branches ($\omega_k \neq 0$, $k \to 0$), where s denotes the number of (inequivalent) atoms in the (primitive) unit cell, $\nu = 1, 2 ... d \cdot s$, see Fig.11.

The quantization of uncoupled oscillators, Eq. (56), is almost trivial. The state of each oscillator (labelled by k) is fixed by quantum numbers $n_k = 0, 1, 2...$, hence

$$E(\{n_k\}) = \sum_k \hbar \omega_k \left(n_k + \frac{1}{2} \right) . \tag{57}$$



a) b)

Figure 11: Structure and Brillouin–zone (a), and phonon dispersion curves (b) for potassium (bcc, one atom per primitive unit cell). Along the horizontal axis we plot q, $q/\sqrt{2}$, and $q/\sqrt{3}$ for the $(1,0,0)$, $(1,1,0)$, and $(1,1,1)$ directions, respectively. According to Cowley et al.[33]

This is already of the form of Eq. (52), and we may identify $\epsilon(k) = \hbar\omega_k$ with the energy of the quasiparticles which are called phonons.

To describe arbitrary phonon states or interaction processes between phonons it is convenient to use creation and anihilation operators $\widehat{a}_k, \widehat{a}_k^\dagger$ rather than $\widehat{P}_k, \widehat{Q}_k$.

$$\widehat{a}_k = \frac{m\omega_k \widehat{Q}_k + i\widehat{P}_k}{\sqrt{2m\hbar\omega_k}}, \quad \left[\widehat{a}_k, \widehat{a}_{k'}^\dagger\right] = \delta_{kk'} \,. \tag{58}$$

These are also called ladder operators as their repeated application on $|n>$ creates the "ladder" of stationary states $n = 0, 1, \ldots$, where $a^+ \mid n >= \sqrt{n+1} \mid n+1 >$, $a \mid n >= \sqrt{n} \mid n-1 >$ "climb" up/down the ladder by one "rung".

$$\widehat{u}_j = \sum_k \sqrt{\frac{\hbar}{2Nm\omega_k}} e^{ikja} (\widehat{a}_{-k}^\dagger + \widehat{a}_k) \,, \tag{59}$$

$$\widehat{H} = \sum_k \hbar\omega_k \widehat{a}_k^\dagger \widehat{a}_k \,. \tag{60}$$

The zero point energy of the oscillators has been omitted as it is not relevant for the dynamics of the system.

Note, there are three different types of particles in the game:

- N coupled "bare" particles of mass m described by $\widehat{p}_j, \widehat{u}_j$,
- N uncoupled harmonically bound particles of unit mass described by $\widehat{P}_k, \widehat{Q}_k$,
- phonons of unlimited number described by $\widehat{a}_k, \widehat{a}_k^\dagger$. In addition, we can consider phonon states which are not even eigenstates of the phonon number operator (see example below).

$$\hat{N} = \sum_k \widehat{a}_k^\dagger \widehat{a}_k \, . \tag{61}$$

For example, we consider two particular phonon states:

One–phonon state: $| \, \phi(k) >= \sum_k \phi(k) | 1_k > = \sum_k \phi(k) \widehat{a}_k^\dagger | 0 >.$

For notational simplicity, $|0 >= |\{n_k\} >$ with $n_k = 0$ for all k. $\widehat{a}_k^\dagger|0 >= |1_k >$ represents a steady state of the oscillator #k in excited state $n_k = 1$, all other oscillators being in the ground state. By construction, $|\phi(k) >$ is an eigenstate of the phonon number operator with eigenvalue 1: $\widehat{N}|\phi(k) >= 1|\phi(k) >$. The time-evolution of this state is $e^{-i\omega_k t}|1_k >$, hence $\phi(k) \rightarrow \phi(k,t) = \phi(k) e^{-i\omega_k t}$ which may be interpreted as wave function of a phonon (-wave packet) in momentum space.[§] For such a state, the expectation value of the position operator of mass #j is $< \phi|\widehat{u}_j|\phi >= 0$ for all times so that it cannot be the quantum analog of a classical wave, it is "quantum noise".

α–state: $|\alpha >= \sum_{n=0}^{\infty} e^{-\frac{1}{2}|\alpha|^2} \frac{\alpha^n}{\sqrt{n!}} |n >.$

Here k is fixed, $n \equiv n_k$, and will be suppressed for notational simplicity, and $\alpha = |\alpha| e^{i\varphi}$ denotes a complex number. Again, the time evolution of $| \, \alpha >$ is easy to find just by replacing α by $\alpha(t) = \alpha \cdot e^{-i\omega t}$. Remarkably, these states describe almost classical (wave-like) motion of the masses in the chain

$$< \alpha(t)|u_j|\alpha(t) > \propto |\alpha| \cos(kja - \omega_k t - \varphi) \, . \tag{62}$$

Hence, $|\alpha|$ and φ fix the amplitude and phase of the wave. α–states are not eigenstates of the phonon number operator and the expectation value and uncertainty are

$$< \alpha|\hat{N}|\alpha >= |\alpha|^2 \, , \quad \Delta N = |\alpha| \, . \tag{63}$$

For large amplitudes $\Delta N / < \hat{N} > \rightarrow 0$. In addition, $\Delta u_j \Delta p_j = \frac{\hbar}{2}$, withy time–independent uncertainties. Thus, in real space, $|\alpha >$ describes a Gaussian wave–packet. Although these states have been already introduced by Schrödinger they

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[§] In contrast to massive quantum particles it is not possible, however, to define a wave function in position space. The reason is that for phonons (or photons) $\omega \propto |k|$, which does not permit a Fouriertransformation from k to r space, see Landau–Lifshitz[14] (Vol. 4).

are nowadays called “coherent” states, Glauber–states, or just α–states. In quantum optics they play a fundamental role for the description of laser radiation and coherence phenomena.[34]

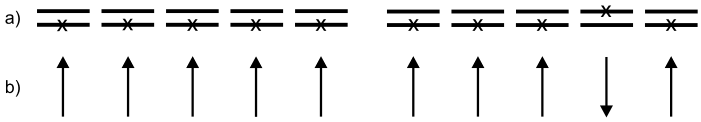

Figure 12: Interacting two–level systems (a) and their pseudo–spin analogon (b). Left: ground state, right: a localized excited state.

B. Excitons

Excitons are propagating electronic exitations in matter. Traditionally, one considers two limiting cases:

- Frenkel–excitons are almost localized atomic or molecular excitations in molecular crystals with little coupling to neighbouring units.
- Wannier–excitons, on the other hand, are loosely bound hydrogen-like electron-hole pairs in semiconductors. These pairs are delocalized over many lattice sites so that a continuum description is possible.

For simplicity, we consider only Frenkel–excitons and approximate the spectrum of molecular excitations by two–level systems, see Fig.12a.

As the Coulomb interaction between the molecules is isotropic, the coupled molecules are described by a Heisenberg model for (pseudo-) spin $\frac{1}{2}$

$$\hat{H} = \sum_j \frac{1}{2}\epsilon_0 \widehat{\sigma}_{jz} - \sum_{ij} J_{ij} \widehat{\sigma}_i \widehat{\sigma}_j \, , \tag{64}$$

where $\widehat{\sigma}_i \widehat{\sigma}_j$ denotes the scalar product of the spin vector operator with Pauli–matrices $(\widehat{\sigma}_x, \widehat{\sigma}_y, \widehat{\sigma}_z)$ at site j. The broken symmetry of the ground states is evident from Fig.12b.

Due to the interaction, the excitation of an isolated molecule (as described by a spin flip at site j) may spread off to neighbouring sites. To bring Eq.(64) to the quasiparticle form Eq. (52), we first transform to exciton creation/annihilation operators $\widehat{b}_j^\dagger, \widehat{b}_j$ by the Holstein–Primakoff transformation[30] (omitting the site index for notational simplicity)

$$\widehat{\sigma}^{(\pm)} = \widehat{\sigma}_x \pm i\widehat{\sigma}_y \, , \quad \widehat{\sigma}^{(+)} = (1 - \widehat{b}^\dagger \widehat{b})^{1/2} \widehat{b}, \quad \widehat{\sigma}^{(-)} = \left(\widehat{\sigma}^{(+)}\right)^\dagger \, . \tag{65}$$

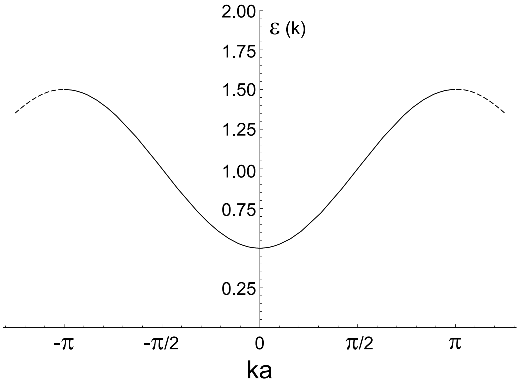

Figure 13: Energy (quasi–)momentum relation of Frenkel–excitons. (Dimensionless quantities, $\epsilon_0 = 1, h_1 = 0.25$.)

Operators at different sites commute. From $[\widehat{\sigma}_j^{(+)}, \widehat{\sigma}_{j'}^{(-)}] = 4\widehat{\sigma}_{zj}\delta_{jj'}$ we obtain $[\widehat{b}_j, \widehat{b}_{j'}^\dagger] = \delta_{jj'}$, hence $\widehat{b}_j, \widehat{b}_{j'}^\dagger$ describe bosonic excitations.

$$\widehat{H}(\widehat{b}^\dagger, \widehat{b}) = \sum_{j=1}^{N} \epsilon_0 \, \widehat{b}_j^\dagger \widehat{b}_j + \sum_{jj'} h_{jj'} \, \widehat{b}_j^\dagger \widehat{b}_{j'} \, \ldots \tag{66}$$

Higher order terms in $\widehat{b}_j, \widehat{b}_j^\dagger$ describe interactions between excitons which can be omitted at low exciton densities. Due to the long–range structure of the Coulomb–interaction many contributions to the coupling elements $h_{jj'}$ have to be taken into account in a realistic description.[35]

In crystals $h_{ij'} = h_{j-j'}$ discrete Fourier–transformation (i.e. transformation to Bloch states)

$$\widehat{b}_j = \sum_k \frac{1}{\sqrt{N}} e^{ikja} \, \widehat{a}_k \,, \qquad \left[\widehat{a}_k, \widehat{a}_{k'}^\dagger\right] = \delta_{kk'} \tag{67}$$

diagonalizes the exciton Hamiltonian, Eq. (66)

$$\widehat{H}(\widehat{a}^\dagger, \widehat{a}) = \sum_k \epsilon(k) \, \widehat{a}_k^\dagger \, \widehat{a}_k + \ldots \,, \qquad \epsilon(k) = \epsilon_0 + \sum_j h_j e^{ikja} \,. \tag{68}$$

In particular, for nearest neighbour interactions, $j = \pm 1$,

$$\epsilon(k) = \epsilon_0 - 2|h_1| \cos ka \,, \tag{69}$$

where, as usual, $h_1 < 0$ is assumed. Eq.(69) is the standard tight–binding result of the linear chain with nearest neighbour couplings, see Fig.13. For a discussion of Wannier–excitons, see e.g. the contributions by Klingshirn.[36,37]

4. Description of Energy Transfer Processes

4.1. States, Processes, and Reversible Dynamics

Processes are described as transitions between states (labelled by ψ). In a state all physical quantities (= observables) have a definite (expectation) value which will be denoted by $< G >_\psi$. Note, this definition does not necessarily imply that $< G >_\psi$ is "sharp", i.e. has vanishing uncertainty $\Delta G = 0$, where $\Delta G = \sqrt{< G^2 > - < G >^2}$.

There are two distinct classes of states:

- pure (or ideal) states which have zero entropy
- mixed (or statistical) states of nonzero entropy.

Irreversibility and loss of coherence are intimately connected with increase of entropy. Hence, the transformation of pure states into mixed states plays a fundamental role in the description of energy transfer processes in macroscopic systems.

According to the dogma of classical physics there are (infinitely many pure) states in which <u>all</u> observables have a sharp value. Hence, $\Delta G \neq 0$ is always caused by errors, either in the state preparation or in the measurement of G. In quantum physics the situation is different. There are particular states in which a <u>specified</u> observable G has sharp values, $\Delta G = 0$. These states are the eigenstates of $\widehat{G}$: $\hat{G}|\psi >= g|\psi >$. But there are no states in which $\Delta G_n = 0$ for $\underline{\text{all } \widehat{G}_n}$. Therefore, $\Delta G_n \neq 0$ is not necessarily caused by errors!

In classical mechanics pure states are specified by the values of coordinates and velocities (or momenta) of all particles which defines a point in phase space: $\psi = (p, q) = (p_1, q_1; p_2, q_2; \ldots)$. G is a function of (p, q), and $< G >_\psi$ is just the functional value of G. The dynamics of these states is governed by the Hamilton-equations of motion

$$\dot{p}(t) = \{H, p\} = -\frac{\partial H(p,q)}{\partial q}\,, \quad \dot{q}(t) = \{H, q\} = \frac{\partial H(p,q)}{\partial p} \tag{70}$$

which underline the central role of the Hamiltonian (= energy) as the generator of time-evolution. Mixed states, on the other hand, are a statistical mixture of pure states and are described by a positive definite, normalized phase space density $\rho(p, q) \geq 0$

$$< G >= \iint G(p,q)\rho(p,q)\, dp\, dq, \qquad \iint \rho(p,q)\, dp\, dq = 1\,. \tag{71}$$

The dynamics of mixed states, $\rho(p, q) \to \rho(p, q, t)$ is governed by the Liouville–equation

$$\frac{\partial \rho(p,q,t)}{\partial t} + \{H, \rho\} = 0\,, \tag{72}$$

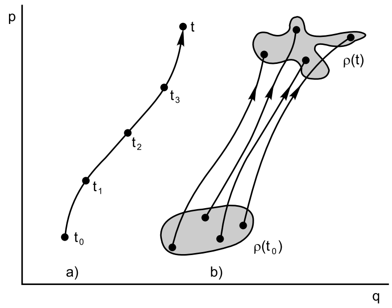

Figure 14: Time evolution in classical mechanics: (a) pure state, (b) mixed state which represents a bundle of trajectories.

which follows from Eq.(70) as each phase space point initiates an individual trajectory, see Fig.14. In particular, for a single particle in one–dimension we have

$$\frac{\partial \rho(p,x,t)}{\partial t} + v\frac{\partial \rho}{\partial x} + F\frac{\partial \rho}{\partial p} = 0\,, \tag{73}$$

where v is the velocity and $F = -V'(x)$ the force acting on the particle.

In quantum mechanics pure states are specified by state-vectors $\mid \psi >$ [or wave functions $\psi(x,t)$], observables are described by hermitian operators $\widehat{G}$, and the (expectation) value of $\widehat{G}$ is defined by

$$< G >_\psi = < \psi|\widehat{G}|\psi > = \int \psi^*(x,t)\,\widehat{G}\,\psi(x,t)dx\,. \tag{74}$$

The dynamics of pure states is determined by and the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)> = \widehat{H}|\psi(t)> \ . \tag{75}$$

A mixed state, as in classical physics, is a statistical mixture of pure states, where the phase space density is replaced by a density operator

$$\widehat{\rho}(t) = \sum \rho_n|n><n|\,, \quad \sum \rho_n = 1\,, \quad \rho_n \geq 0\,. \tag{76}$$

$\mid n >$ denote an arbitrary set of state–vectors (which might not even be orthogonal!) with (real) positive weights ρ_n, and the expectation value Eq.(74) is replaced by

$$< G > = tr\left(\widehat{\rho}\widehat{G}\right) = \sum_\alpha < \alpha|\widehat{\rho}\,\widehat{G}|\alpha > = \sum_n \rho_n \ < n|\widehat{G}|n >\,, \tag{77}$$

where α labels an arbitrary base. The last part of Eq. (77) can be interpreted as the “usual” quantum average of $\widehat{G}$ with respect to the pure states $|n>$ with a classical average with weights $\rho_{\mathbf{n}}$ put on top. Eventually, we mention that the density operator

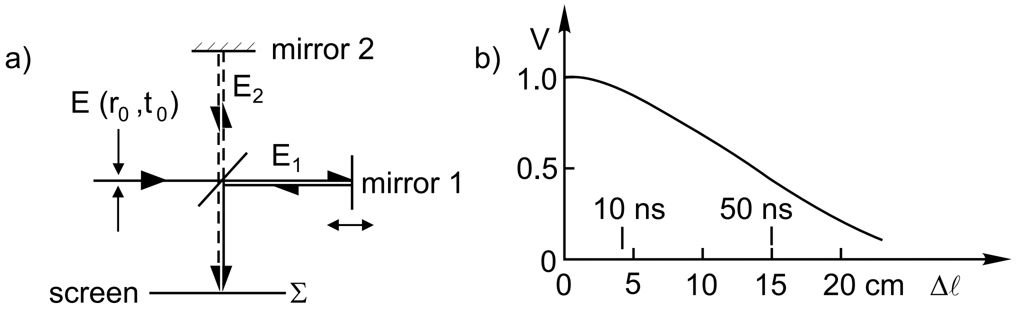

Figure 15: Schematic of the Michelson interferometer (a) and visibility curve of the red Cadmium line (b). Δl is the difference in path length of mirrors 1,2. $\Delta t = \Delta l/c$ is the coherence time. According to Born and Wolf.[44]

of a pure state $|\psi >$ is the projector $\widehat{\rho} = |\psi >< \psi|$. The dynamics of a quantum mixture follows the v. Neumann–equation[¶]

$$\frac{\partial \widehat{\rho}(t)}{\partial t} + \frac{i}{\hbar}[\widehat{H}, \widehat{\rho}] = 0\,. \tag{78}$$

Mixed states have nonzero entropy

$$S = -k_B tr\left(\widehat{\rho}\,\ell n \widehat{\rho}\right)\ . \tag{79}$$

In the classical case the trace is replaced by phase–space integration. Noticeable, both the Liouville– and the v. Neumann equations describe reversible processes, $\frac{\partial S(t)}{dt} = 0$! We are able to describe states of nonzero entropy, but not irreversibility!

4.2. Coherence and Correlation

The notion of coherence originates from optics where it describes space-time correlations of the electromagnetic field. Familiar consequences are the appearance of interference fringes in a double–slit experiment or other oscillatory phenomena. A prominent instrument to study coherence phenomena is the Michelson-interferrometer, see Fig.15.

$$\begin{aligned}
&\text{Field on screen } \Sigma\text{:} \quad && \mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 \quad && = \quad C\left[\mathcal{E}_{in}(\mathbf{r}_0, t_0 + \tau_1) + \mathcal{E}_{in}(\mathbf{r}_0, t_0 + \tau_2)\right] \\
&\text{Intensity:} && I = |\bar{\mathcal{E}}|^2 && = \quad C^2\left[G(1,1) + G(2,2) + 2\Re G(1,2)\right] \qquad (80) \\
&\text{Correlator:} && G(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) && = \quad \left\langle \mathcal{E}^{(-)}(\mathbf{r}_2, t_2)\mathcal{E}^{(+)}(\mathbf{r}_1, t_1) \right\rangle
\end{aligned}$$

[¶] At first sight Eq.(78) looks like a Heisenberg equation of motion of $\widehat{\rho}(t)$. However, the sign is different and $\hat{\rho}(t)$ is in the Schrödinger-picture! In fact, Eq. (78) expresses the conservation of probability $\frac{d\widehat{\rho}(t)}{dt} = 0$.

C is a suitable constant and $\mathcal{E}^{(\pm)}$ contains the positive/negative frequency components of the electrical field ($\propto exp(\mp i\omega_k t)$. In a mode-expansion (e.g. free propagation of the EMF from a star to the earth) we have

$$\mathcal{E}(\mathbf{r},t) = \sum_{\mathbf{k}} A_{\mathbf{k}} e^{i(\mathbf{kr}-\omega_{\mathbf{k}}t)} + cc = \mathcal{E}^{(+)}(\mathbf{r},t) + \mathcal{E}^{(-)}(\mathbf{r},t) \tag{81}$$

so that the correlator at equal space points, $\mathbf{r}_2 = \mathbf{r}_1$, can be written as

$$G(t_2,t_1) = \sum_{\mathbf{k}} |A_{\mathbf{k}}|^2 \, e^{-i\omega_{\mathbf{k}}(t_2-t_1)} \, . \tag{82}$$

For example, for a Gaussian line of width $\Delta\omega$ centered at ω_0 the normalized correlation function becomes ($G(t,t) = 1$):

$$\begin{aligned} A(\omega) &= \exp\left[-\frac{(\omega-\omega_0)^2}{2\Delta\omega^2}\right] , & (83) \\ G(t_2,t_1) &= e^{-i\omega_0(t_2-t_1)} \exp\left[-\frac{1}{2}[\Delta\omega(t_2-t_1)]^2\right] . & (84) \end{aligned}$$

For such a line the fringe–contrast ("visibility") in the Michelson interferometer (see Fig.15) is defined by

$$V = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \exp\left[-\frac{1}{2}[\Delta\omega(t_2-t_1)]^2\right] , \tag{85}$$

where the explicit result refers to the Gaussian line. Eqs.(83,84) explicitely show an example of the famous Wiener-Khinchine theorem: Filtering in **k**-space (=restriction of frequencies and/or **k**-directions) increases the coherence–time or coherence–area (perpendicular to **k**). This is just a property of the Fourier–transformation, $\Delta t \propto 1/\Delta\omega$, etc.

Analogous to optics, coherence can be defined for any quantity which is additive and displays a phase or has a vector character, e.g. electrical and acoustic "signals", electromagnetic fields, wave–functions, etc. Coherence is intimately connected with reversibility, yet the opposite is not always true. At first sight, a process might appear as fully incoherent or random, nevertheless it may represent a highly correlated pure state. A beautiful example is the spin– (or photon–) echo[27,41] which is related to a superposition of many sinusoidal field components with fixed (but random) frequencies. At $t = 0$ these components have zero phase difference and combine constructively to a nonzero total amplitude. Later, however, they develop large random phase differences and add up more or less to zero so that the signal resembles "noise". Nevertheless, there are fixed phase relations between the components at every time. By certain manipulations at time T a time–reversal operation can be realized which induces an echo at time $t = 2T$, which uncovers the hidden coherent nature of the state.

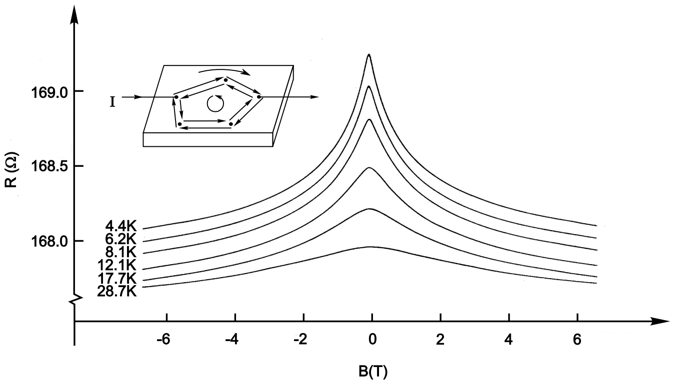

Figure 16: Resistance of a metallic magnesium film as a function of magnetic field. For elastic electron–impurity scattering there are two equivalent time-reversed paths which lead to an increase of the resistance by coherent backscattering ("weak localization"). A magnetic field leads to a phase shift between both paths which uncovers the finite phase–coherence time of the electrons originating from the (temperature dependent) inelastic electron–phonon scattering. According to Bergmann.[45]

Another nice example in this respect, is the phenomenon of "weak localization" of conduction electrons in disordered materials, see Fig.16. Echo phenomena are always strong indications of hidden reversibility and coherence!

Problem:
Consider a sum of many (co–)sinusoidal functions with fixed (but randomly chosen) frequencies ω_n

$$f(t) = \sum_n \cos \omega_n t\,, \quad \omega_n = (1 + r_n)2\pi\,. \tag{86}$$

The distribution of r_n is assumed to have a zero mean with probability $P(r)$.
(a) Study $f(t)$ numerically for a box distribution $P(r) = \Theta(\sigma^2 - r^2)/2\sigma$ and a Gaussian distribution.
(b) Compare with the analytical result

$$f(t) = \langle \cos(1 + r)2\pi t \rangle = \Re \left\{ e^{2\pi i t} \int P(r) e^{2\pi i r t} dr \right\}\,. \tag{87}$$

[Hint: A Gaussian distributed random variable can be generated numerically by summing many random numbers of any distribution (Central Limit theorem)].

4.3. Irreversible Dynamics

The phenomena of irreversibility is ubiquitous in all macroscopic systems. Nevertheless, the old question how to describe irrevesibility and decoherence on a microscopic (reversible) basis has no simple answer and, possibly the final answer has still not been found.[38,39]

Irreversibility, i.e. the increase of entropy with time intimately connected with the transformation of pure states into mixed states. In addition, it is not possible to include dissipative forces in the Hamiltonian itself. Presently, the dogma of theoretical physics is that irreversibility arises from the coupling of a system to its infinite environment ("heat bath") or by the boundary conditions which, in an infinite system, can also spoil time–reversal symmetry. [‖] A real expert in the field of traditional thermodynamics, however, will consider such a "trick" as mean deception!

The dynamics of the total system with Hamiltonian

$$\widehat{H}_{tot} = \widehat{H}_{sys} + \widehat{H}_{bath} + \widehat{H}_{int} \tag{88}$$

obeys the reversible Liouville/v. Neumann equation, where $\widehat{H}_{int}$ describes the interaction between the system and the bath. For electrons in a solid the bath may be realized by the phonon system which is held by a constant temperature T. The task is to eliminate the bath variables from the equations of motion of the total system, and to construct equations for the system of interest. Note, although the basic equations are reversible the dynamics of the system will be not. For finite systems, however, there is always a finite Poincaré recurrence time. Nakajima and Zwanzig[40] have derived a general procedure to eliminate the bath variables, at least in principle, but it is very difficult to do it in practice. The resulting equations are irreversible, non–Markovian, and have a memory behaviour. Some simple examples will be given in Chapter 5. In many cases, however, various approximate treatments are used, some of which will be discussed in more detail in the next sections.

a. Relaxation time approximation.
   Phenomenologically, a relaxation term is added to the Liouville/v. Neumann equations which mimics the system-bath interaction:

$$\frac{\partial \widehat{\rho}(t)}{\partial t} + \frac{i}{\hbar}[\widehat{H}, \widehat{\rho}] = -\frac{1}{\tau}\left(\widehat{\rho}(t) - \widehat{\rho}_{eq}\right) , \tag{89}$$

   where τ is an appropriate relaxation–time and $\widehat{\rho}_{eq}$ describes the equilibrium state. Obviously, this equation is no longer symmetric with respect to time–reversal and, thus, describes irreversible processes. Note, Eq. (89) conserves

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[‖] An example is a lossless coaxial cable with (real) impediance Z and infinite length. At one of its ports, this cable is indistinguishable from an ohmic resistor with resistance Z, although there is no dissipation involved.

the normalization $tr\widehat{\rho}(t) = 1$. In general, $\widehat{\rho}_{eq}$ refers to a local rather than to global equilibrium in order not to violate particle number conservation. The relaxation time approximation is expected to be good for weak coupling and not too small times. A nice application of this approximation has been given by Mermin[43] who included damping in the Lindhard dielectric function $\epsilon(q,\omega)$.

b. Master equation (incoherent limit).
This description considers only the diagonal elements of the statistical operator (with respect to the eigenstates of the isolated system) $P_n(t) =< n|\widehat{\rho}|n >$; nondiagonal elements are considered to be zero.

$$\frac{d}{dt}P_m(t) = \sum_n \left[\Gamma_{mn}P_n(t) - \Gamma_{nm}P_m(t)\right] \tag{90}$$

The transition rates Γ_{mn} can be obtained from the "Golden Rule" and obey the symmetry relation $\Gamma_{mn}\, exp(-E_m/k_BT) = \Gamma_{nm}\, exp(-E_n/k_BT)$, where T is the temperature of the bath.[57]

c. Stochastic Liouville/v. Neumann equations.
The interaction of an electronic system (like excitons) and the phonons in a crystal is approximately treated as a heat bath pushing the electrons or excitons in a stochastic manner. This description is justified if the temperature is not too low, otherwise polaron states are formed. However, it is not possible to take the reaction of the electron or exciton on the phonons into account. There is action but not reaction! For example, for Frenkel–excitons the interaction part of the Hamiltonian Eq.(66) is replaced by

$$H_{int} = \sum_{mn} f_{mn}(t)\widehat{b}^{\dagger}_m\widehat{b}_n\,, \tag{91}$$

where $f_{mn}(t)$ is assumed to descibe a Gaussian stochastic process with zero mean value. The diagonal element $f_{nn}(t)$ describes fluctuation of the exciton energy ϵ at lattice site n, whereas the non-diagonal elements represent the stochastic variations of the (coherent) interaction matrix element $h_{jj'}$ in Eq.(66). For details we refer to the book by Kenkre and Reineker[7] (see p. 120 ff).

d. Kinetic (Boltzmann) equation
We consider a gas of (quasi–) particles with weak short range interactions. Instead of the (classical) phase space distribution function $\rho(\mathbf{r}_1,\mathbf{p}_1\ldots\mathbf{r}_N,\mathbf{p}_N)$ the one–particle distribution function

$$f(\mathbf{r},\mathbf{p},t) = \int\!\!\int \rho(\mathbf{r},\mathbf{p};\mathbf{r}_2,\mathbf{p}_2;\ldots r_N,\mathbf{p}_N;t)\, d\mathbf{r}_2\, d\mathbf{p}_2\ldots d\mathbf{r}_N\, d\mathbf{p}_N \tag{92}$$

is used which obeys the kinetic equation

$$\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial t} + \mathbf{v}(\mathbf{p})\,\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial \mathbf{r}} + \mathbf{F}(\mathbf{p},\mathbf{r})\,\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial \mathbf{p}} = C\,, \tag{93}$$

where $\mathbf{v}$ is the velocity, Eq.(53), and $\mathbf{F}$ an (external) force acting on the particles. Boltzmann had the ingenious idea to approximate the interactions between the particles, as summarized by C, by the concept of collisions, i.e. short range, instantaneous gain–loss processes with no memory to previous states (=Markov–process).

Collision term: $\qquad C = N_{in}(\mathbf{r}, \mathbf{p}, t) - N_{out}(\mathbf{r}, \mathbf{p}, t).$

$N_{in/out}$ count the number of particles scattered in/out $d\mathbf{p}$ at $\mathbf{p}$. It is almost a miracle how this equation has withstood all criticsms and how it could be adapted to quantum mechanics, [f($\mathbf{r}$,$\mathbf{p}$,t) becomes the Wigner–function, in thermal equilibrium, f is the Fermi/Bose function.] In contrast to the Liouville equation, Eq.(93) is no longer symmetric under time–reversal: the *lhs* changes sign whereas the *rhs* does not. Therefore the Boltzmann equation describes irreversible processes. Cohen and Thirring[52] give a historical survey and discussions of the celebrated Boltzmann equation, whereas Landau-Lifshitz[14] (Vol. 10) deal with physical kinetics in the wide sense of the microscopic theory of nonequilibrium processes.

For example, for elastic scattering of electrons by impurities in a metal or semiconductor the collision term becomes[**]

$$C(f) = \int [w(\mathbf{p}' \to \mathbf{p}) f(\mathbf{r}, \mathbf{p}, t) - w(\mathbf{p} \to \mathbf{p}') f(\mathbf{r}, \mathbf{p}, t)] \; d\mathbf{p}' \tag{94}$$

with the intrinsic scattering rate (in Born approximation)

$$w(\mathbf{p} \to \mathbf{p}') = N_{imp} \frac{2\pi}{\hbar} \left| < \mathbf{p}' | V_{imp} | \mathbf{p} > \right|^2 \delta(\epsilon_{\mathbf{p}} - \epsilon_{\mathbf{p}'}) \, . \tag{95}$$

For electron–phonon interaction N_{in}, N_{out} each contain two terms describing the absorption and emission of a phonon,[58] see Fig.9a.

[**] Note that Eq.(94) contains no "blocking" factors $(1-f)$ for final scattering states, in accordance with Kohn and Luttinger,[47] but contrary to naive thinking and many textbooks. The $(1-f)$ cancel if $W\mathbf{k}, \mathbf{k}') = W(\mathbf{k}', \mathbf{k})$ is symmetric but would lead to erroneous results for skew–scattering.[48] In an independent particle description no products $f_{\mathbf{p}} f_{\mathbf{p}'}$ can occur as these describe particle–particle interactions. The situation is different for (inelastic) electron–phonon interaction where the blocking factors are necessary.

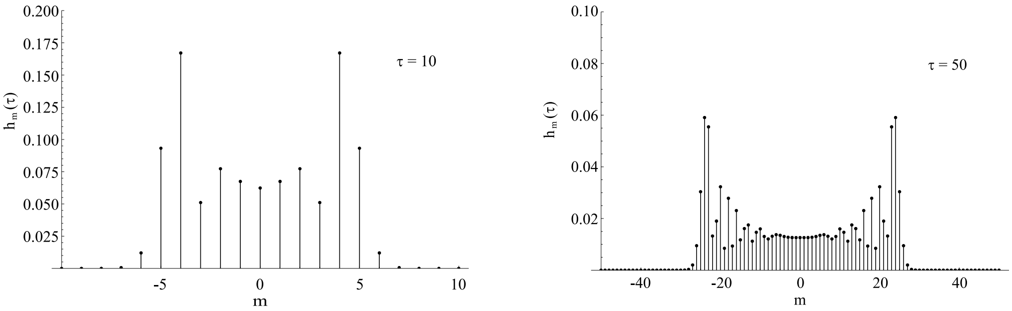

Figure 17: Spatio–temporal evolution of the energy per site, $h_m(t)$. Local momentum excitation at $m = 0$. According to Vasquez-Marquez et al.[49]

4.4. Examples

A. Linear chain

Energy transport in a classical monoatomic chain, see Fig.10, has been considered already by Hamilton and Schrödinger[46] and more recently by Vasquez-Marquez et al.,[49] who derived analytical results for the energy transport. In particular, for momentum excitation at $t = 0$ and site $m = 0$ the local energy $[h_m(t) = \rho_E(ma, t)]$

$$h_m(t) = \frac{P_0^2}{2M}\left\{J_{2m}^2(\tau) + \frac{1}{2}J_{2m-1}^2(\tau) + \frac{1}{2}J_{2m+1}^2(\tau)\right\} \tag{96}$$

shows an oscillating, nonexponential decay in time to neighbouring sites. $J_m(\tau)$ denotes a Bessel–function,[51] $\tau = \omega_L t$ is the dimensionless time, $\omega_L = \sqrt{4\frac{D}{M}}$ is the largest phonon frequency, and M is the mass of the particles.

Note, the main peaks in $h_m(\tau)$ resemble those of the string, see Fig.2, yet there is no trailing edge and the energy between the peaks propagates off rather slowly. From the mean square displacement $< m^2 > \rightarrow (\bar{c}\tau)^2$ we deduce a (dimensionless) mean propagation velocity $\bar{c} = 1/\sqrt{2}$, where $\bar{c}^2$ is just the mean square of the group velocity.

B. Two–level–system

We study a system with two base states represented by

$$|1 >= \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2 >= \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{97}$$

and a coupling parameterized by a real, positive constant ϵ. The Hamiltonian of this system and its eigenstates $|I >$, $|II >$ and energies $E_I = -\epsilon$, $E_{II} = \epsilon$ are given by

$$H = \begin{pmatrix} 0 & -\epsilon \\ -\epsilon & 0 \end{pmatrix}, \quad |I >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |II >= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{98}$$

A realization of such a system is a spin 1/2 in a magnetic field in x-direction, $\widehat{H} = -\mu_B \mathcal{B}\cdot\widehat{\sigma}$ ($\widehat{\sigma} = (\widehat{\sigma}_x, \widehat{\sigma}_y, \widehat{\sigma}_z)$ denote the Pauli-matrices) or a particle in a double-well potential. Further examples can be found in the Feynman–Lectures[16] (Vol. III).

(a) Schrödinger dynamics

The Schrödinger equation for $|\psi(t)>$

$$|\psi(t)>= c_1(t)|1> + c_2(t)|2> \tag{99}$$

yields two coupled differential equations for the amplitudes

$$i\hbar\dot{c}_1(t) = -\epsilon c_2(t)\,, \quad i\hbar\dot{c}_2(t) = -\epsilon c_1(t) \tag{100}$$

which can be easily solved by insertion. For $|\psi(0)>= |1>$ we obtain

$$c_1(t) = \cos(\frac{\omega_0}{2}t)\,, \quad c_2(t) = i\sin(\frac{\omega_0}{2}t)\,, \tag{101}$$

where $\omega_0 = 2\epsilon/\hbar$ is the transition frequency between levels I,II. As a result, the probability finding the system in (base) states $|1>$, $|2>$ and expectation values of the spin vector are

$$\begin{aligned}
P_1(t) &= |c_1(t)|^2 = \cos^2(\frac{\omega_0}{2}t)\,, & (102)\\
P_2(t) &= |c_2(t)|^2 = \sin^2(\frac{\omega_0}{2}t)\,, & (103)\\
<\widehat{\sigma}_x> &= 2\Re c_1^*(t)c_2(t) = 0\,, & (104)\\
<\widehat{\sigma}_y> &= 2\Im c_1^*(t)c_2(t) = \sin(\omega_0 t)\,, & (105)\\
<\widehat{\sigma}_z> &= |c_1(t)|^2 - |c_2(t)|^2 = \cos(\omega_0 t)\,. & (106)
\end{aligned}$$

Note, that $<\sigma_x>$ is time independent as $\hat{\sigma}_x$ commutes with $\hat{H}$ and, thus, is conserved.

(b) Relaxation dynamics

It is convenient to expand the density operator with respect to the eigenstates $|I>$, $|II>$ of $\hat{H}$ because $\widehat{\rho}_{eq}$ is diagonal in this representation

$$H = \begin{pmatrix} -\epsilon & 0 \\ 0 & \epsilon \end{pmatrix}\,, \quad \widehat{\rho}_{eq} = \frac{1}{Z}\begin{pmatrix} e^{\beta\epsilon} & 0 \\ 0 & e^{-\beta\epsilon} \end{pmatrix}\,, \tag{107}$$

$Z = \exp(\beta\epsilon) + \exp(-\beta\epsilon)$ is the partition function and $\beta = 1/(k_BT)$ is the inverse temperature.

The general form of the density operator is

$$\widehat{\rho}(t) = \begin{pmatrix} A & B \\ B^* & 1-A \end{pmatrix}\,. \tag{108}$$

A is real, $0 \le A \le 1$, whereas B may be complex. Initially, $\widehat{\rho}(0) = |1><1|$, hence $A(0) = B(0) = 1/2$. Writing Eq. (89) in a matrix form, we obtain for the $(1,1)$ and $(1,2)$ components of $\widehat{\rho}$

$$\begin{aligned} \dot{A}(t) + \gamma A(t) &= \frac{\gamma}{Z} e^{\beta\epsilon} \,, && (109) \\ \dot{B}(t) + (\gamma - i\omega_0)\, B(t) &= 0 \,, && (110) \end{aligned}$$

where $\gamma = 1/\tau$. As a result,

$$\begin{aligned} A(t) &= \frac{1}{2} e^{-\gamma t} + \frac{1}{Z} e^{\beta\epsilon} \left[1 - e^{-\gamma t}\right] \,, && (111) \\ B(t) &= \frac{1}{2} e^{-\gamma t} e^{i\omega_0 t} \,. && (112) \end{aligned}$$

In order to compare with the previous example we have to transform vectors ψ and matrices M (base $|1>, |2>$) to $\bar{\psi}$, $\bar{M}$ (base $|I>$, $|II>$):

$$\psi = \widehat{U}\bar{\psi} \,, \quad M = \widehat{U}\bar{M}\widehat{U}^{\dagger} \,, \quad \widehat{U} = \sqrt{\frac{1}{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \,. \tag{113}$$

For example, $\bar{\sigma}_x = \sigma_z$, $\bar{\sigma}_y = -\sigma_y$, $\bar{\sigma}_z = \sigma_x$, hence

$$\begin{aligned} <\widehat{\sigma}_x> &= \left[1 - e^{-\gamma t}\right] \tanh(\beta\epsilon) \,, && (114) \\ <\widehat{\sigma}_y> &= e^{-\gamma t} \sin(\omega_0 t) \,, && (115) \\ <\widehat{\sigma}_z> &= e^{-\gamma t} \cos(\omega_0 t) \,, && (116) \\ P_1(t) &= \frac{1}{2} \left[1 + e^{-\gamma t} \cos(\omega_0 t)\right] \,, && (117) \\ P_2(t) &= \frac{1}{2} \left[1 - e^{-\gamma t} \cos(\omega_0 t)\right] \,, && (118) \\ <\widehat{H}> &= -\epsilon <\widehat{\sigma}_x> \,. && (119) \end{aligned}$$

(c) Master equation

As states $|1>, |2>$ have equal energy the transition rates must be equal, $\Gamma_{12} = \Gamma_{21} = \Gamma$ and so that the master equations Eqs.(90) become

$$\dot{P}_1(t) = \Gamma(P_2 - P_1) \,, \quad \dot{P}_2(t) = \Gamma(P_1 - P_2) \,. \tag{120}$$

By conservation of probability, $P_1 + P_2 = 1$ these equations can be easily solved, thus

$$P_1(t) = \frac{1}{2} \left[1 + e^{-2\Gamma t}\right] \,, \quad P_2(t) = \frac{1}{2} \left[1 - e^{-2\Gamma t}\right] \,. \tag{121}$$

Results of coherent, fully incoherent, and relaxation dynamics are displayed in Fig.18.

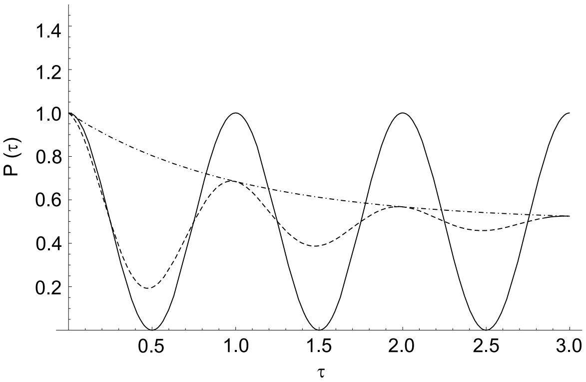

Figure 18: Dynamics of the two–level–system. Coherent (solid line), relaxing (dashed line), and fully incoherent motion (dashed–dotted line).

C. Exciton chain

(a) Schrödinger dynamics

Instead of expanding the wave function into the stationary states of Eq.(68), we try to solve the (time–dependent) Schrödinger equation for a single exciton directly. In site representation, the amplitudes $c_m(t)$ of the state vector

$$|\psi(t)>=\sum_m c_m(t)|1_m> , \quad c_m(0)=\delta_{m,0} \tag{122}$$

obey the coupled set of differential equations

$$i\hbar\dot{c}_m(t)=\epsilon_0 c_m(t)-h_1\left[c_{m+1}(t)+c_{m-1}(t)\right] . \tag{123}$$

Using an "innocent looking" Ansatz

$$c_m(t)=i^m e^{-i\epsilon_0 t/\hbar}\mathcal{C}_m(\tau) , \quad \tau=\omega_0 t , \quad \omega_0=|h_1|/\hbar \tag{124}$$

Eq.(123) reveals a well known recursion relation of Bessel–functions[51]

$$\begin{aligned} \mathcal{C}'_m(\tau) &= \frac{1}{2}\left[\mathcal{C}_{m-1}-\mathcal{C}_{m+1}(\tau)\right] , &(125)\\ \mathcal{C}_m(\tau) &= \alpha J_m(\tau+\tau_0)+\beta Y_m(\tau+\tau_0) , &(126)\end{aligned}$$

α, β, τ_0 being constants, but $\beta=0$ as $C_m(\tau)$ must be finite. Imposing $c_m(0)=\delta_{m,0}$ as an initial condition, we obtain

$$C_m(t)=i^m e^{-i\epsilon_0 t/\hbar}J_m(\omega_0 t) , \quad P_m(t)=|C_m(t)|^2 \tag{127}$$

For large times $\tau \gg 1$, $P_m(t)\rightarrow 2\cos(\omega_0 t-m\pi/2-\pi/4)/(\pi\omega_0 t)$ displays a damped, oscillatory behaviour, see Fig.19. In contrast to the two–level–system there is no Poincaré recurrence time because of the infinite system size. Note also, the decay of the oscillations is not due to dissipation. The mean square displacement is wave–like, $< (ma)^2 > (t) = (\bar{c}t)^2$, where the square of the propagation velocity $\bar{c} = a\omega_0/\sqrt{2}$ is identical with the mean square of the exciton group velocity.

(b) Master equation

Motivated by the previous success we intend to solve the set of Master–equations

$$\frac{dP_m(t)}{dt} = \Gamma\left[(P_{m+1} - P_{m-1}) + (P_{m+1} - P_{m-1})\right] \tag{128}$$

by an appropriate Ansatz

$$P_m(t) = e^{-\tau}\mathcal{Z}_m(\tau)\,, \quad \tau = 2\Gamma t\,. \tag{129}$$

Indeed, this reveals a recursion relation for (modified) Bessel–functions[51]

$$\begin{aligned} \mathcal{Z}'_m(\tau) &= \frac{1}{2}\left[\mathcal{Z}_{m+1}(\tau) + \mathcal{Z}_{m-1}(\tau)\right]\,, \qquad (130)\\ \mathcal{Z}_m(\tau) &= \alpha I_m(\tau+\tau_0) + \beta K_m(\tau+\tau_0)\,. \qquad (131) \end{aligned}$$

Again, $\beta = 0$ as P_m must be finite. Imposing $P_m(0) = \delta_{m,0}$ the solution is

$$P_m(t) = e^{-2\Gamma t} I_m(2\Gamma t)\,. \tag{132}$$

For large times $\tau \gg 1$, $P_m(t) \to 1/(\sqrt{4\pi\Gamma}\,t)$, which resolves the diffusive character of the process, $< (ma)^2 >= 2Dt$, $D = \Gamma a^2$ is the diffusion constant.

Problems:

1.) Calculate the entropy, Eq.(79), of the damped two–level system as a function of time. [Hint: Evaluate the trace in eigenbasis of $\widehat{\rho}(t)$].

2.) Show that the coherent and fully incoherent dynamics of a two–level system can be described in terms of a generalized master equation with a memory kernel $\Gamma(t-t')$

$$\frac{dP_1(t)}{dt} = \int \Gamma(t-t')\left[P_2(t') - P_1(t')\right] dt'\,. \tag{133}$$

Which $\Gamma(t-t')$ corresponds to the relaxing system?

3.) An interesting, yet pathological case (of Ca,b), is a cluster of molecules with equal coupling strength between all N sites. [Hint: use $\sum_n c_n$ =const, $\sum_n P_n = 1$].

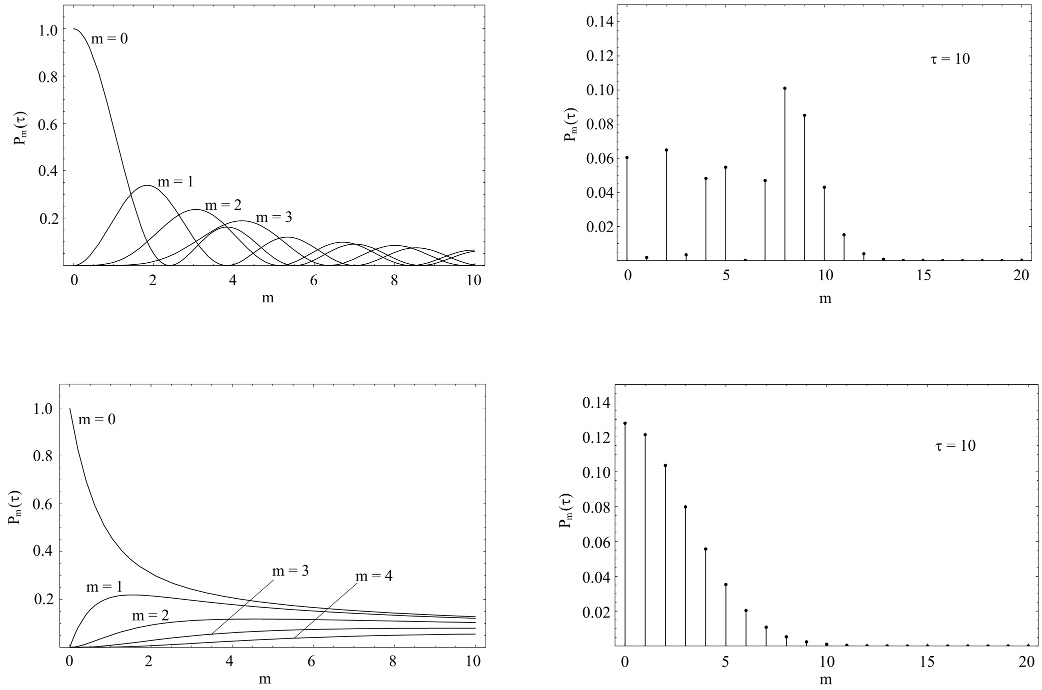

Figure 19: Spatio–temporal evolution of the energy per site in the excitonic chain $P_m(\tau)$ (= probability finding an exciton at m). (Top) coherent, (bottom) incoherent motion, according to Eqs.(127,132).

D. *Gas of (quasi–) particles*

(a) Approach to equilibrium

We consider a homogeneous, dilute gas of hard disks in two–dimensions. At $t = 0$ all particles are located on a square grid and have the same magnitude but random directions of momentum (velocity). By numerical integration of the Newton–equations,[53] $f\,d\mathbf{p}$ is obtained by counting the number of particles in $d\mathbf{p}$. As time proceeds, the particle collisions tend to realize a Maxwellian distribution

$$f_0(\mathbf{p}) = f_0 \exp\left[-\frac{\mathbf{p}^2}{2mk_BT}\right] \tag{134}$$

which is accompanied by a monotonous increase of entropy. The time interval for reaching equilibrium roughly corresponds to 200 collisions. However, this state is highly correlated and apparently only describes "molecular chaos": Reversing all particle velocities after 50 or 100 collisions reproduces the initial state, see Fig. 20. Therefore,

$$S = -k_B \iint f(\mathbf{p},\mathbf{r},t)\,\ell n\, f(\mathbf{p},\mathbf{r},t)\,d\mathbf{r}d\mathbf{p} \tag{135}$$

obviously does not give the correct (change) of entropy. (Note the difference between Eq.(79) and Eq.(135).) For longer times, however, numerical errors come into play

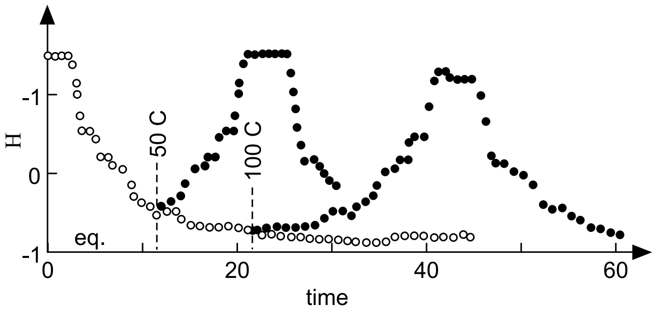

Figure 20: Eta-function $H = -S/k_B$) of a system of 100 hard disks in a square with periodic boundary conditions showing kinetic (open circles) and antikinetic (full circles) evolutions for velocity inversions taking place at 50 and 100 collisions. According to Orban and Bellemans.[53]

and destroy reversibility.

An analytical solution of the Boltzmann equation is very difficult as the collision integral $C(f)$ is nonlinear in f. In the vicinity of thermal equilibrium, however, a linearized description by a relaxation time approximation is possible (homogeneous conditions, no external forces)

$$\frac{\partial f(\mathbf{p},t)}{\partial t} = -\frac{f - f_0}{\tau} \tag{136}$$

so that the distribution approaches equilibrium in an exponential manner.

(b) Noninteracting particles

We consider (quasi–) classical point–like particles without mutual interaction moving in a random array of stationary scatterers ("pinball machine"). Realizations of such a model are

- slow neutrons in a heavy medium,
- gas mixture with large mass ratio (=Lorentz gas),
- electrons in "anti-dot" semiconductor systems,
- elastic electron impurity scattering in a metal.

We study the case of electrons in a metal or doped semiconductor. In thermal equilibrium, $C(f_0) = 0$, where f_0 is the Fermi–function

$$f_0(\mathbf{p}) = \frac{1}{1 + \exp\left[\frac{\epsilon_{\mathbf{p}} - \mu}{k_B T}\right]}\,, \tag{137}$$

and μ is the chemical potential (Fermi–energy). An applied electrical field (parallel to the z-axis) $\mathcal{E}_z(t) = \mathcal{E}_0 \Re \exp(-i\omega t)$ drives the system out of equilibrium. For isotropic, elastic scattering of electrons by impurities the scattering kernel is independent of the scattering angle Ω so that the kinetic equation becomes

$$\frac{\partial f(\mathbf{p},t)}{\partial t} + (-e)\mathcal{E}_0 e^{-i\omega t}\frac{\partial f(\mathbf{p})}{\partial \mathbf{p}} = \frac{1}{\tau}\int \frac{1}{4\pi}\left[f(\mathbf{\Omega}',t) - f(\mathbf{\Omega},t)\right] d\mathbf{\Omega}' \,. \tag{138}$$

In linear order with respect to $\mathcal{E}_0$, $f = f_0(\mathbf{p}) + f_1(\mathbf{p})\exp(-i\omega t)$, we obtain for the first order correction.

$$f_1(\mathbf{p}) = \frac{ev_z}{\gamma - i\omega}\frac{\partial f_0(\mathbf{p})}{\partial \mathbf{p}}\mathcal{E}_0 + \frac{< f_1(\mathbf{p}) >}{\gamma - i\omega} \,. \tag{139}$$

$< f_1(\mathbf{p}) >$ denotes the angular average of $f_1(\mathbf{p})$ which can be calculated selfconsistently from the above equation. $\gamma = 1/\tau$. (The current induced by the external field, however, does not depend on $< f_1(\mathbf{p}) >$). As a result, we have

$$j_z(\omega)e^{-i\omega t} = \frac{-e}{V}\sum_{\mathbf{p}} v_z\, f_1(\mathbf{p})e^{-i\omega t} = \sigma_D(\omega)\mathcal{E}_0\, e^{-i\omega t} \,, \tag{140}$$

$$\sigma_D(\omega) = \frac{ne^2}{m}\frac{1}{\gamma - i\omega} \,. \tag{141}$$

$\sigma_D(\omega)$ is the Drude–conductivity. For a detailed study of the Lorentz–model see Hauge's article.[54]

(c) Plasma oscillations

A one-component plasma consists of one type of mobile particles (electrons) which are imbedded in an homogeneous positive neutralizing background (density ρ_+). As the Coulomb interaction between the particles is long–range it cannot be treated by the concept of collisions. A reasonable approximation, however, can be formulated within the concept of a mean field $\mathcal{E}_{mf}$, which describes the coherent motion of the particles. $\mathcal{E}_{mf}$ is treated on equal footing with an applied electrical field (if any),

$$\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial t} + \mathbf{v}\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial \mathbf{r}} + (-e)\mathcal{E}_{mf}(\mathbf{r},t)\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial \mathbf{p}} = 0 \,, \tag{142}$$

$$\text{div}\,\mathcal{E}_{mf}(\mathbf{r},t) = \frac{1}{\epsilon_0}\left[\rho_+(\mathbf{r},t) + \rho_-\right] \,, \quad \text{curl}\,\mathcal{E}_{mf}(\mathbf{r},t) \approx 0 \,. \tag{143}$$

These are the Landau–Vlassov equations. We are looking for a self–sustained plane wave solution of the linearized equations of the form

$$f(\mathbf{r},\mathbf{p},t) = f_0(\mathbf{p}) + f_1(\mathbf{p})e^{i(\mathbf{qr} - \omega_q t)} \,. \tag{144}$$

(Note the difference between wave vector $\mathbf{q}$ and electron momentum $\mathbf{p}$.) For small wave vectors q, the dispersion of the plasma wave becomes

$$\omega_p(q) = \omega_p + \frac{\beta}{2\omega_p}q^2 \ldots \,, \tag{145}$$

where $\omega_p^2 = ne^2/(m\epsilon_0)$ is the square of the plasma frequency, $\beta = 3v_F^2/5$, and v_F is the Fermi velocity of the electrons. For $q \to 0$, there is no damping of the plasma wave in the Landau–Vlassov approximation. For wave vectors $q \approx k_F$, however, plasmons can decay into electron–hole pairs (Landau–damping), although Eq.(142) is invariant under time–reversal! For a survey on plasmons, see, e.g., Ref.[55]

5. Memory Functions and non–Markovian Behaviour

5.1. *Memory function concept*

The dynamics of closed systems as studied in the previous sections is determined by a set of first order differential equations with respect to time. Given the state at time t_0 these equations determine the state at all later times, see e.g. the Hamiltonian equations Eq.(70). In addition, in classical mechanics damping may often be phenomenologically included by introducing a friction-force $-\gamma_0\dot{x}$. For instance, for a particle with mass M in a potential $V(x)$ the Newton–equation reads

$$M\ddot{x}(t) = -M\gamma_0\dot{x} - \frac{\partial V(x)}{\partial x} + f(t)\,, \tag{146}$$

where $f(t)$ is an external force. Actually, the friction–force has to be supplemented by an additional fluctuating force $\xi(t)$, (with zero mean) which represents e.g. the collisions of molecules impinging on the (heavy) particle. This is the Langevin formulation which not only describes the damped average motion but also the fluctuations around it, see van Kampen.[57]

In a more detailed description of open systems the heat bath is often modelled by a system of harmonic oscillators and the bath degrees of motion are eliminated to construct an equation of motion for the system (particle) alone. This will be illustrated by two examples in the following sections. In such a description the reaction of the bath on the system particle is also taken into account which leads to an equation of the form

$$M\ddot{x} + \int_{-\infty}^{t} M\gamma(t-t')\,\dot{x}(t')\,dt' + \frac{\partial V(x)}{\partial x} = f(t)\,. \tag{147}$$

This equation is nonlocal in time and the memory function $\gamma(t-t')$ determines how far the "history"of $x(t')$ ($t' < t$ according to causality) influences the present $x(t)$. With $\gamma(t-t') = \gamma_0\delta(t-t')$ we are back at Eq.(146). Note, $x(t_0)$ and $\dot{x}(t_0)$ do no longer determine the state of the particle, at least not in the same sense as it has been used in Chapters 3. and 4. Additional assumptions for $t \to -\infty$ are needed. Equation (147) describes a non-Markovian process which will be discussed in the next section.

As an example, we consider a harmonic oscillator with frequency ω_0 under the action of a monochromatic force, $f(t) = f_0 \cos(\omega t)$. As a result, the solution is

$$
\begin{aligned}
x(t) &= \Re\left[x(\omega) f_0 e^{-i\omega t}\right] , && (148)\\
x(\omega) &= \frac{1}{M}\frac{1}{\omega_0^2 - \omega^2 - i\Gamma(\omega)\omega} , && (149)\\
\Gamma(\omega) &= \int_0^\infty \gamma(t) e^{i\omega t} dt = \Gamma_1(\omega) + i\Gamma_2(\omega) . && (150)
\end{aligned}
$$

Note, memory effects do not only lead to a frequency dependent scattering rate ($= \Gamma_1$) but to a shift in the resonance frequency ($= \Gamma_2$), too.

Memory effects have an interesting consequence on the frequency dependence of conduction electrons (mass m, density n, $\omega_0 = 0$). Expressing the electron current as $j(t) = -en\dot{x}(t)$, $f(t) = -e\mathcal{E}(t)$, we obtain for the conductivity

$$
\sigma(\omega) = \frac{ne^2}{m}\frac{1}{\Gamma(\omega) - i\omega} , \qquad (151)
$$

which is a generalization of the Drude result Eq.(141), see Fig.22. Deviations the measured conductivity of conduction electrons from the Drude result are always indications of memory effects. For experimental evidence, see, e.g., measurements by Dressel et al.[56] on some organic conductors.

In quantum physics, the inclusion of dissipation requires more care because quantum systems are described by a Hamiltonian which, in the absence of time dependent external potentials, ensure the conservation of energy. On the other hand, dissipative forces cannot be included in the Hamilton itself. A successful and rather general approach is by the concept of an (infinite) reservoir and elimination of the reservoir degrees of freedom. For details and applications we recommend the book by Dittrich et al.[50] which gives an excellent introduction and overview on the relation of quantum transport and dissipation. Master and Boltzmann equations with memory kernels have been respectively studied by Kenkre[5,42] and Hauge.[54]

A. Caldeira–Leggett model

As an example how to eliminate the bath variables we consider a classical particle of mass M and coordinate q, which is bilinearly coupled to a set of harmonic oscillators ("bath"), see Ingold's article in Ref.[50] (p. 213).

$$
\begin{aligned}
H &= H_s + H_{bath} + H_{int} , && (152)\\
H_s &= \frac{p^2}{2M} + V(q) , && (153)\\
H_{bath} &= \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2 , && (154)\\
H_{int} &= -q \sum_i c_i x_i + q^2 \sum_i \frac{c_i^2}{2m_i\omega_i^2} , && (155)
\end{aligned}
$$

with suitable constants for c_i, ω_i, m_i. This model has been used by several authors and is nowadays known as the Caldeira–Leggett model. The equations of motion of the coupled system are:

$$M\ddot{q} + V'(q) + q\sum_i \frac{c_i^2}{m_i\omega_i^2} = \sum_i c_i x_i \,, \tag{156}$$

$$\ddot{x}_i + \omega_i^2 x_i = \frac{c_i}{m_i} q(t) \,. \tag{157}$$

As the bath represents a system of uncoupled oscillators their equation of motion can be easily solved in terms of the (unknown) driving term $\sim q(t)$.

$$x_i(t) = x_i(0)\cos(\omega_i t) + \frac{p_i(0)}{m_i}\sin(\omega_i t) + \int_0^t \frac{c_i}{m_i\omega_i}\sin[\omega_i(t-t')]q(t')dt' \,. \tag{158}$$

Inserting this solution into the Newton-equation of the particle, we obtain

$$M\ddot{q}(t) + \int_0^t M\gamma(t-t')\dot{q}(t')\,dt' + V'(q) = \xi(t) \,, \tag{159}$$

where $\gamma(t-t')$ is the damping kernel (memory function) and $\xi(t)$ is a fluctuating force (which depends on the initial conditions of the bath variables and is not stated here)

$$\gamma(t) = \frac{2}{\pi}\int_0^\infty \frac{J(\omega)}{\omega}\cos(\omega t)d\omega \,, \tag{160}$$

$$J(\omega) = \pi\sum_i \frac{c_i^2}{2Mm_i\omega_i}\delta(\omega-\omega_i) \,. \tag{161}$$

For a finite number of bath oscillators the total system will always return to its initial state after a finite (Poincaré) recurrence time or may come arbitrarily close to it. For $N \to \infty$, however, the Poincaré time becomes infinite simulating dissipative behavior (see also Chapter 4.3.). We therefore first take the limit $N \to \infty$ and consider the spectral density of bath modes as a continous function. Frictional damping, $\gamma(t) \sim \gamma_0\delta(t)$, is obtained for $J(\omega) \sim \gamma_0\omega$. A more realistic behavior would be the "Drude" form

$$J(\omega) = \gamma_0\omega\frac{\gamma_D^2}{\omega^2+\gamma_D^2} \,, \quad \gamma(t) = \gamma_0\gamma_D e^{-\gamma_D t} \,, \tag{162}$$

which behaves as in the friction case for small frequencies but goes smoothly to zero for $\omega > \gamma_D$, see Fig.21.

B. Rubin model

A rather nontrivial yet exactly solvable model is obtained by a linear chain (see Chapters 3.7.A and 4.4.A), with one mass replaced by a particle of (arbitrary) mass

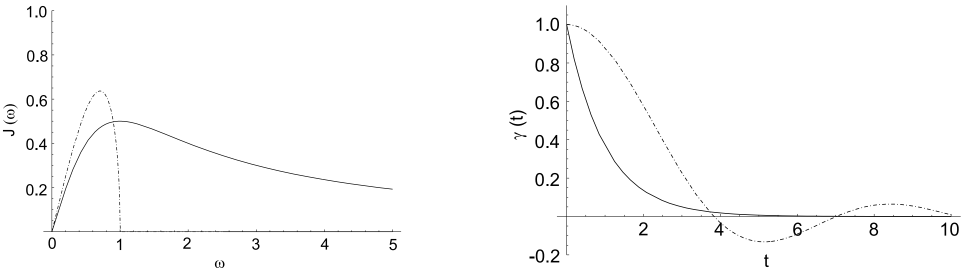

Figure 21: Spectral density of the bath oscillators (left) and memory functions (right). Solid lines: Caldeira–Leggett model with a Drude form, dashed dotted lines: Rubin model. (Dimensionless quantities, $M_0/M = 1$).

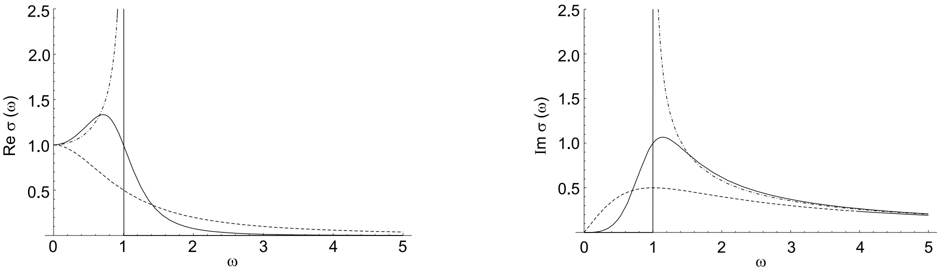

Figure 22: Real and imaginary parts of the electrical conductivity for the Caldeira–Leggett and Rubin models. Dashed lines: Drude model, other notations as in Fig.21.

M_0, see Fig.10. The left and right semi–infinite wings of the chain serve as a bath to which the central particle is coupled. As a result the damping kernels are

$$\gamma(t) = \frac{M_0}{M}\omega_L \frac{J_1(\omega_L t)}{t}\,, \tag{163}$$

$$\Gamma(\omega) = \frac{M_0}{M}\begin{cases} \sqrt{\omega_L^2 - \omega^2} + i\omega\,, & |\omega| < \omega_L\,, \\ i\frac{\omega_L^2 sgn(\omega)}{\omega_L + \sqrt{\omega^2 - \omega_L^2}}\,, & |\omega| > \omega_L\,, \end{cases} \tag{164}$$

$$J(\omega) = \Re\Gamma(\omega) = \frac{M_0}{M}\sqrt{\omega_L^2 - \omega^2}\,\Theta(\omega_L^2 - \omega^2)\,, \tag{165}$$

where $J_1(x)$ is a Bessel–function. In contrast to the Drude case the memory function shows oscillations and decays merely algebraically for large times, see Fig. 21.

$$\gamma(t) \to \frac{M_0}{M}\sqrt{\frac{2\omega_L}{\pi}}\frac{\sin[\omega_L t - \pi/4]}{t^{3/2}}\,. \tag{166}$$

The oscillations in $\gamma(t)$ are connected with the upper cut–off in $J(\omega)$ at the maximum phonon frequency ω_L. For details, see Fick and Sauermann[40] (p. 255).

5.2. Stochastic Processes and Non-Markovian Behavior

Many phenomena depend on time in an extremely complicated way which is far beyond the possibility of observation and calculation. A possibility to circumvent this dilemma in theoretical physics is to replace the system by a suitable chosen ensemble of systems all having the same equations but different initial microstates. Therefore, state variables are turned into stochastic variables. By additional drastic assumptions about the nature of the stochastic processes this does simplify matters enormously. In many cases, these processes are modelled by Markovian–processes, which (in appropriate variables), lead to equations of motion which are local in time. Examples are the derivation of the master and Boltzmann equations. In many cases, however, memory effects show up which indicate non–Markovian behaviour, see e.g. Wegener's article[8] in this volume. To elucidate the physics of these phenomena and their description we follow van Kampen[57] who gives an excellent introduction and overview on stochastic processes in physics and chemistry.

The definition of a stochastic variable X consists of specifying

- the set of all possible values ("sample space") and
- the probability distribution $P(X)$ over this set

$$P(x) \geq 0\,, \qquad \int P(x)\,dx = 1\,. \tag{167}$$

The average of $f(X)$ is defined as

$$< f(X) >= \int f(x)\,P(x)\,dx\,. \tag{168}$$

(For discrete X, the integral is understood as a sum). A prominent example is the Gauss-distribution

$$P(X) = \sqrt{\frac{1}{2\pi\sigma}}e^{-\frac{1}{2\sigma}x^2}\,, \quad < x^2 >= \sigma\,. \tag{169}$$

A stochastic process is defined as a function of X by some mapping $X \to Y$ which is a function of time

$$Y_X(t) = f(X,t)\,. \tag{170}$$

Such a quantity is also called a random function. On inserting for X one of its possible values x, an ordinary function of time results, which is called a sample function or a realization of the process, see Fig. 23. Averages are defined by

$$< Y_X(t) > \;=\; \int Y_X(x,t)\,P_X(x)\,dx\,, \tag{171}$$

$$< Y_X(t_1)Y_X(t_2) > \;=\; \int Y_X(x,t_1)\,Y_X(x,t_2)\,P_X(x)\,dx\,. \tag{172}$$

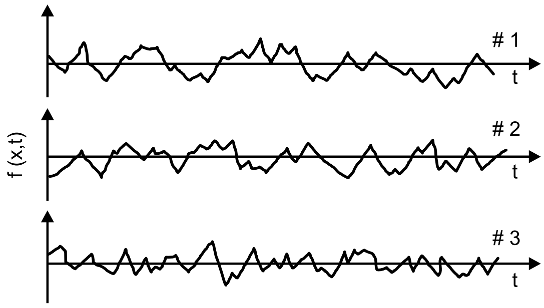

Figure 23: Schematic of sample functions.

The latter is [apart from a redefinition of $Y_X(t) \to Y_X(t) - < Y_X(t) >$] the autocorrelation function of $Y_X(t)$.

A stochastic process can also be specified by a hierarchy of distribution functions $P_n(y_1,t_1;y_2,t_2;\dots;y_n,t_n)$, $n = 1,2,\dots$. $P_1(y,t)$ is the probability density for $Y_X(t)$ to take the value y at time t, P_2 is the joint probability that $Y_X(t)$ has the value y_1 at t_1 and y_2 at t_2, etc. Functions P_n are symmetric in all arguments y_i, t_i but $t_i \neq t_k$ is implied.

The conditional probability $P_{1|1}(y_2,t_2|y_1,t_1)$ is the probability density for $Y_X(t)$ to take the value y_2 at t_2, given that its value at t_1 is y_1. More generally one may fix the values at k different previous times $t_1, t_2, \dots t_k$ and ask for the joint probability of Y_X at ℓ other later times $t_{k+1}, \dots t_{k+\ell}$. This leads to the general definition of the conditional probability

$$P_{\ell|k}(k+1;\dots k+\ell|1,2,\dots k) = \frac{P_{k+\ell}(1,2,\dots k+\ell|1,2,\dots k)}{P_k(1,2\dots k)}\,, \tag{173}$$

where "i" is a shorthand for y_i, t_i. Like P_1, P_n, $P_{\ell|k}$ is non–negative and normalized. (Notice the difference in sequence of the arguments in joint and conditional probabilities). A process is called a Gaussian process if all its P_n are (multivariate) Gaussian distributions. For a stationary process all P_n depend on time–differences alone and $P_1(y,t)$ is time–independent.

A Markov–process is defined as a stochastic process for any set of successive times $t_1 < t_2 < \dots t_n$ has the property

$$P_{1|n-1}(y_n,t_n|y_1,t_1;\dots y_{n-1},t_{n-1}) = P_{1|1}(y_n,t_n|y_{n-1},t_{n-1})\,. \tag{174}$$

In short: Markov processes don't have a memory.

A Markov process is fully determined by $P_1(y,t)$ and $P_{1|1}(y_2,t_2|y_1,t_1)$ $(t_2 > t_1)$

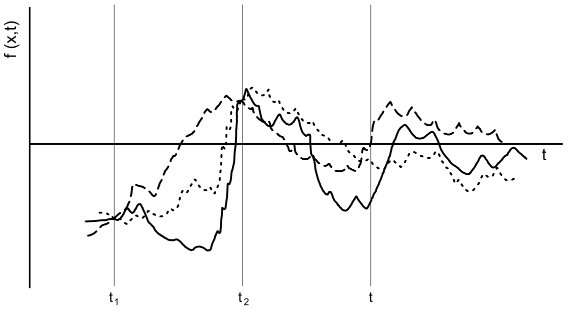

Figure 24: Schematic of sample functions contributing to the conditional probability.

as the whole hierarchy of joint probabilities P_n can be reconstructed from them, e.g.

$$\begin{aligned} P_1(y_2,t_2) &= \int P_{1|1}(y_2,t_2|y_1,t_1)\,P(y_1,t_1)\,dy_1\,, && (175)\\ P_2(y_1,t_1;y_2,t_2) &= P_{1|1}(y_2,t_2|y_1,t_1)\,P_1(y_1,t_1)\,, && (176)\\ P_3(y_1,t_1;y_2,t_2;y_3,t_3) &= P_2(y_1,t_1;y_2,t_2)\,P_{1|2}(y_3,t_3|y_1,t_1;y_2,t_2)\,, && (177)\\ &= P_1(y_1,t_1)P_{1|1}(y_2,t_2|y_1,t_1)P_{1|1}(y_3,t_3|y_2,t_2)\,. && (178) \end{aligned}$$

Continuing this algorithm one finds successively all P_n. This property makes Markov processes so managable and, fortunately, Markov processes are by far the most important stochastic processes in physics and chemistry.

One of the best known Markov processes is the Wiener–process which describes the diffusive behavior of the position of a Brownian particle

$$\begin{aligned} P_1(y_1,0) &= \delta(y_1)\,, && (179)\\ P_{1|1}(y_2,t_2|y_1,t_1) &= \frac{1}{\sqrt{4\pi D(t_2-t_1)}}\exp\left[-\frac{(y_2-y_1)^2}{4D(t_2-t_1)}\right]\,. && (180) \end{aligned}$$

In particular, we have for the time–dependent (i.e. non–stationary) probability, finding the particle at y at time t

$$P_1(y,t) = \frac{1}{\sqrt{4\pi Dt}}e^{-\frac{y^2}{4Dt}}\,. \qquad (181)$$

An example of a stationary Markov–process is the Ornstein–Uhlenbeck process which describes the velocity of the Brownian particle, see van Kampen.[57]

The concept of a Markov process is not restricted to one–component processes but applies to processes with r components as well. However, if one ignores $s > 0$ components of an r component Markovian process, the resulting $r - s$ component stochastic process will – in general – not be Markovian! The art of the physicist is to find such variables that are needed to make the description (approximately) Markovian.

In physics “non–Markovian” is used almost synonymously for“memory behaviour”, yet the reader should beware of several pitfalls. Quoting van Kampen[57]

> *When a physicist talks about a process he/she normally refers to a certain phenomenon involving time. Concerning a process in this way it is meaningless to ask whether or not the process is Markovian, unless one specifies the variables to be used for its description ...*
> *The criterion Eq.(174) is a condition on all distributions P_n of the hierarchy. It is impossible to aver that a process is Markovian if only information about the first few P_n is available...*
> *Surprisingly, any deterministic process, like the Hamiltonian dynamics in phase space, Eq.(70), or the v.Neumann dynamics, Eqs.(78,89), is Markovian...*
> *Sometimes "non–Markovian" equations of the form*
>
> $$\frac{\partial P(t)}{\partial t} = \int_0^t G(t,t')\,P(t')\,dt' \tag{182}$$
>
> *are produced, yet one cannot be sure that the earlier values of $P(t)$ are indispensable for knowing its future...*

Problem:
Consider the non–Markovian Eq.(147) with an exponential memory function $\gamma(t) = \gamma_0\gamma_D \exp(-\gamma_D t)\Theta(t)$. Show by differentiation that this equation can be transformed to a system of three first order differential equations with no memory for the composite variable $\xi = (x, \dot{x}, \ddot{x})$.

6. Final Remarks

In this article the standard equations and their typical solutions and properties for (energy) transport in condensed matter were provided. We found that reversibility and coherence are often – yet not always – accompanied by oscillations in the physical quantities of interest. A large number of important questions and techniques, however, have only been touched and perhaps not even mentioned. For example, for semiconductors the standard theory to describe coherent phenomena are the Semiconductor–Bloch equations which describe the coherent motion of the interband amplitude as well as the electron/hole kinetics, see Haug and Koch.[58] A short survey about such problems has been given previousely[27] and is not repeated here. The interplay between transport and coherence is most pronounced in systems where extremly short length scales ($\sim$ 1nm) or ultra fast time scales ($\sim$ 1fs) play a crucial role. It turns out to be very difficult to make significant generalizations of the Boltzmann equation to go beyond the limits set by the "old master" himself. To properly describe phenomena of this kind, a quantum theory of nonequilibrium processes is needed which has only recently been developed. For details, we refer to Fick and Sauermann,[40] Dittrich et al.,[50] and Haug and Jauho.[59]

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