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Author's Review

A Statistical Description of Molecular Dynamical Processes in Liquids. Application to FIR Absorption Spectroscopy*

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The basic physical concepts concerning the derivation and validity of the generalized fluctuation-dissipation theorem (FDT) as revealed in an earlier paper[11] are discussed. It is shown that dissipation of irradiation within the framework of Kubo's linear response theory is mainly due (i) to the short-time behavior of the coupling operator of a system with the irradiation field, (ii) to the spontaneous fluctuations concerning the statistical operator in the microscopic time scale, and (iii) to the explicit introduction of the coupling of the systems with the thermal bath in Kubo's formalism, as proposed by van Vliet.

As a result, the statistical operator becomes time dependent in the shorttime range. Within Kubo's microscopic theory of irreversible processes the generalized FDT also delivers a microscopic interpretation of Prigogine's theorem of minimum entropy production (TMEP).

1. INTRODUCTION

In recent contributions to the statistical mechanics of nonequilibrium states much progress has been achieved especially by investigating the *fluctuation-dissipation theorem* (FDT) in its different versions[1-10]. For some spectroscopic methods which probe the dynamics of molecular motions in liquids (and in general in disordered condensed media) Kubo's theory[1,2] is especially suitable as has also been shown in our first paper in this series[11].

In this paper the dynamics of a *molecular* (and, therefore, *not macroscopic*) quantity **M** will be considered. As an example **M** will be indentified with the permanent electric dipole moment of a rather small polar molecule like CH_3CN in the liquid phase. The quantity **M** is assumed to be coupled with an external electromagnetic field through the semiclassical interaction Hamiltonian, Eq. (1), as Kubo proposed in his *linear response theory* (LRT)[1,2].

1.1. *Utilization of FIR Absorption Spectra*

For reasons of clarity and illustration we confine the following considerations to the physical context of far-infrared (FIR) absorption spectroscopy of dilute solutions of polar molecules in non-polar solvents. It is well-known,

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that FIR-absorption spectra occur mainly due to rotational relaxation of the polar molecules[11–19].

In such cases the relation

$$\tau_M \cong 2\pi/\omega_{max} \equiv t_{max}$$

holds true, where ω_{max} denotes the frequency of the irradiation field at the maximum of the measured absorption band, and τ_M is the *rotational relaxation time* of **M**. Thus, there are no »well-defined« of »stable« rotational quantum states for the molecules under consideration *during time intervals of the order of* t_{max}. The interaction between FIR-irradiation and spectroscopic probe, therefore, cannot lead to well-defined quantum-mechanical excited states. As a matter of fact the »absorbed« irradiation energy will be dissipated, at least if the time intervals of the order of t_{max} are considered. From this follows that the necessary conditions for the validity of the so-called *adiabatic-approximation* (see ref. 20, §§ 11 and 125) are not fulfilled. This approximation for the calculation of the rate of irradiation energy dissipation, however, is successfully used within many physical problems. For the case of FIR spectroscopy, however, the inadequacy of the adiabatic approximation must be examined carefully (see Sec. 2.2).

1.2. *Van Vliet's and van Kampen's Criticism Concerning LRT*

As van Vliet states: »Linear response theory speaks of dissipation and associated transport coefficients, but nowhere is the dynamics commensurate with dissipation introduced.«; and additionally: »In the formalism (of LRT) as it stands no dissipation is manifest.« (cf. 21, p. 1353 and abstract, respectively). This statement can be verified in the case of irradiation interacting with the quantum systems dealt with (see Sec. 3.1). It can be shown that there is irradiation energy dissipation in LRT if the coupling operator **M** shows non-Markovian behavior[25]. This is again the case if one considers a microscopic **M** within time intervals of the order τ_M since now *memory effects* concerning the dynamical behavior of **M** are of importance[26–28, 3, 16–17]. As van Vliet asserts, the coupling of the quantum system with the heat bath must be explicitly taken into the formalism[21]. This seems to be important in the molecular (i. e. microscopic) time scale, since then it is easy to show that the density operator of the ensemble cannot be a *static* quantity (see Sec. 3.3). Furthermore we can show that in this case there is dissipation in LRT.

In this context van Kampen's critisism concerning Kubo's linearization of the density operator[23–24] must also be pointed out. This linearization cannot be generally justified. However in the case of FIR-spectroscopy this procedure is acceptable due to the fact that the time interval during which the linearization must work is small, i. e. of the order of the relaxation time τ_M, which is typically of the order 10^{-12} s or even smaller under normal conditions (cf. 21, p. 1353). Nevertheless, Kubo's linearization of the density operator shows an important weakness: it introduces a »repeated randomization« into the calculations; as van Kampen states: »The effect of randomization is simulated by the linear approximation.« (cf. ref. 23 p. 282).

This remark will be of some importance in our considerations concerning fluctuations of the density operator in the microscopic time scale (see Sec. 3.3).

2. ON THE FLUCTUATION-DISSIPATION THEOREM (FDT) IN KUBO'S FORMALISM AS APPLIED TO MOLECULAR QUANTITIES

Now we discuss some fundamental assumptions concerning the derivation of the generalized FDT[11].

2.1. *On the Hamiltonian*

We have considered a dissipative system (with the unperturbed Hamiltonian $\mathbf{H}_o$) interacting with an external driving system (radiation with the Hamiltonian $\mathbf{H}_{ex}$). In the so-called dipole approximation the interaction Hamiltonian of the whole system is[10]

$$\mathbf{H}_I = -\mathbf{M} \cdot \mathbf{E} \tag{1}$$

M and **E** are two characteristic quantities of the partial systems with the Hamiltonians $\mathbf{H}_o$ and $\mathbf{H}_{ex}$, respectively.

Usually the dissipative system possesses a large number of degrees of freedom and a quasi-continuous energy spectrum. On the other hand the driving system or external disturbance has relatively few degrees of freedom and a very high degree of excitation. The coordinates and momenta of the external disturbance as well as of the quantity **E** can be considered, therefore, as being essentially some classical functions of time[10], and the perturbed Hamiltonian attains the form

$$\mathbf{H} = \mathbf{H}_o - \mathbf{M} \cdot E(t) \tag{2}$$

As stated in Sec. 1.1, we consider the special case where the operator **M** represents a *microscopic* quantity, e. g. the *permanent* electric dipole moment of a molecule like CH_3CN. The dissipative system consists of one polar molecule (or: of one polar molecule and a small number of non-polar solvent molecules surrounding it). As is well known, in Kubo's original presentation of LRT[1-2] the coupling of the quantum system with the thermal bath is not taken into account by the Hamiltonian but is only indirectly introduced into the formalism through the *linearization*

$$\varrho \to \varrho_{eq}$$

of the exact density operator ϱ, as mentioned in Sec. 1.2., where ϱ_{eq} represents the equilibrium *canonical* density operator

$$\varrho_{eq} = \exp(-\beta \cdot \mathbf{H}_o)/\mathrm{Tr}\exp(-\beta \cdot \mathbf{H}_o)$$

However, as van Vliet states, »If this is to be more than a mathematical artifice, we must physically change the system so it becomes open and in interaction with the heat bath« (cf. ref. 21 p. 1353). We do not introduce this coupling explicitly into the Hamiltonian, since we are not interested in improving the LRT but only in its application. This improvement of LRT, in connection with the so-called van Hove limit, has been carried out successfully by van Vliet[21-22].

Nevertheless, the importance of this coupling in the physical context of molecular FIR spectroscopy is beyond dispute; the reason being that the interaction of a polar molecule (and its cage of surrounding solvent molecules) with the environmental dielectricum cannot be considered as being »very small«. As we will show in Sec. 3.3.1. this coupling naturally leads to a time dependent or »fluctuating« density operator in the microscopic time scale; hence van Kampen's critisism on the linearization of ϱ seems to be also confirmed in the special case under consideration.

2.2. *Rate of Dissipation and Adiabatic Approximation*

The irradiation energy dissipation per time unit has to be evaluated by means of the operator of the time dependent perturbation, which in the simplest case reads

$$H_{\mathrm{I}} = -\vec{M} \cdot \vec{E} \tag{3}$$

(For simplicity's sake we discuss the problem in classical-mechanical terms.)

The applied electric field perturbing the equilibrium within disordered condense molecular matter is assumed to be of sinuidal character in the FIR spectral region

$$\vec{E} = \vec{E}_{\mathrm{o}} \cdot \exp{(i\omega t)}$$

where $\omega \cong 10^{11} \ldots 10^{13}\ \mathrm{s}^{-1}$.

In organic liquids of small and uncharged molecules the first relaxation time τ_{R}, e. g. of molecular reorientation, is of the order of one picosecond. Hence

$$\tau_{\mathrm{R}} \cong \nu^{-1} \equiv 2\pi/\omega$$

and during a time interval $\Delta t \cong \tau_{\mathrm{R}}$ the perturbation energy will be changed by

$$\Delta H_{\mathrm{I}} = -\Delta\vec{M} \cdot \vec{E} - \vec{M} \cdot \Delta\vec{E} \tag{4}$$

Thus

$$\dot{H}_{\mathrm{I}} = -\dot{\vec{M}} \cdot \vec{E} - \vec{M} \cdot \dot{\vec{E}} \tag{5}$$

The ensemble average $\langle \dot{H}_{\mathrm{I}} \rangle$ of $\dot{H}_{\mathrm{I}}$ delivers the rate of irradiation energy dissipation $Q\,(\omega)$ by the molecular quantum system under consideration.

Two notes of caution may be helpful in avoiding confusion. In the first step one might think that the term $\vec{M} \cdot \dot{\vec{E}}$ *completely determines* the rate of energy dissipation Q. This assumption could be based on the well known theorem of mechanics which states that for the total Hamiltonian H of the material system holds $\mathrm{d}H/\mathrm{d}t = \partial H/\partial t$. In our case only the interaction term H_{I} exibits an explicit time dependence and thus

$$Q \equiv \left\langle \frac{\mathrm{d}H}{\mathrm{d}t} \right\rangle = \left\langle \frac{\partial H_{\mathrm{I}}}{\partial t} \right\rangle = -\langle \vec{M} \cdot \dot{\vec{E}} \rangle \tag{6}$$

Nevertheless it would be wrong to assume that this »derivation« is *always* correct. Eq. (6) holds true only if *adiabatic processes* are considered, as e. g. Landau and Lifschitz have shown very clearly (cf. ref. 20 §§ 125 and 11). An important necessary condition for the validity of Eq. (6) is that $\vec{E}\,(\mathrm{t})$ varies very slowly in time compared with the characteristic relaxation time of the (quantum) system. This condition is fulfilled in many cases, e. g. NMR, ESR and dielectric relaxation in liquids.

However, in the case of FIR spectroscopy this condition is violated: As mentioned in Sec. 1.1, the period T_E of $\vec{E}\,(t)$ is now of the same order of magnitude as the reorientational relaxation time τ_M of $\vec{M}$. Naturally, even in cases where the »adiabatic condition« is not fulfilled, Eq. (6) is approximately valid, e. g. if that $\vec{E}\,(t)$ oscillates very fast compared with τ_M. In other words: if $T_E \ll \tau_M$ then the molecular quantity $\vec{M}$ can be approximately considered to be a »constant« during time intervals of the order of T_E since then $0 \cong \langle \dot{\vec{M}} \cdot \vec{E}\,(t) \rangle \ll \langle \vec{M} \cdot \dot{\vec{E}} \rangle$ and from Eq. (5) follows Eq. (6) approximately. This physical situation can be found e. g. in the case of UV spectroscopy in fluids and in FIR spectroscopy in the gas phase. Please note that in those cases the absorbed irradiation energy will not be dissipated during time intervals of the order of T_E, but rather leads to well-defined excited quantum states. This process can be reasonably described by quantum mechanics (but not by thermodynamics).

Another remark may also be helpful. Sometimes it is believed that the term $\langle \dot{H}_I \rangle$,

$$\langle \dot{H}_I \rangle = -\langle \dot{\vec{M}} \cdot \vec{E} \rangle - \langle \vec{M} \cdot \dot{\vec{E}} \rangle$$

is *identically* zero, because (i) the first term on the rhs. is the change in the system energy, (ii) the second term is the change in the field energy, (iii) the total system (system plus field) is isolated and, therefore, the total energy cannot decrease. Of course, this argument is correct if processes which conserve energy in the mechanical sense are considered.

However, in connexion with dissipative processes the above »derivation« is absurd: As a matter of fact, that part of field energy being converted into heat *cannot* be represented by the *system* Hamiltonian (and its ensemble average), since that amount of the field energy causes an increase of the *internal energy* of the *thermal bath*.

2.3. *The Exact FDT in Linear Response Theory*

In the quantum mechanical case it follows from Eq. (5)

$$Q \equiv \langle \dot{\mathbf{H}}_I \rangle = -\langle \dot{\mathbf{M}} \rangle E - \langle \mathbf{M} \rangle \dot{E} \tag{5a}$$

This equation can be derived more formally too. With the aid of the Heisenberg equation of motion for $\mathbf{H}_I$ we get

$$\dot{\mathbf{H}}_I = -\frac{1}{i\hbar}\,[\mathbf{M} \cdot \mathrm{E},\, \mathbf{H}] \quad \frac{\partial}{\partial t}(\mathbf{M} \cdot E)$$

$$= -\frac{1}{i\hbar}\,[\mathbf{M}, \mathbf{H}] \cdot E - \mathbf{M} \cdot \dot{E}$$

$$\equiv -\dot{\mathbf{M}} \cdot E - \mathbf{M} \cdot \dot{E}$$

and consequently (5a) holds.

The two terms of Eq. (5a) have been calculated for the »microscopic« case mentioned in Sec. 1.1.

Because of the fact that the superposition principle is valid within the linear response theory, we can calculate $Q(\omega)$ for a monochromatic external perturbation $E(\omega)$ with frequency ω, which yields[11]

$$Q(\omega) \propto \frac{1}{\hbar} |E_0|^2 \cdot \tanh(\beta\hbar\omega/2) \cdot \{\omega \cdot \hat{C}(\omega) - \omega^{-1} \cdot \hat{C}'(\omega)\} \tag{7}$$

with the abbreviations

$\hat{C}(\omega)$: Fourier transform of the quantum-mechanical time autocorrelation function of the operator $\mathbf{M}$,

$\hat{C}'(\omega)$: Fourier transform of the quantum-mechanical time autocorrelation function of the operator $\dot{\mathbf{M}}$,

$\beta = 1/kT$, where T is the temperature of the heat bath of the ensemble

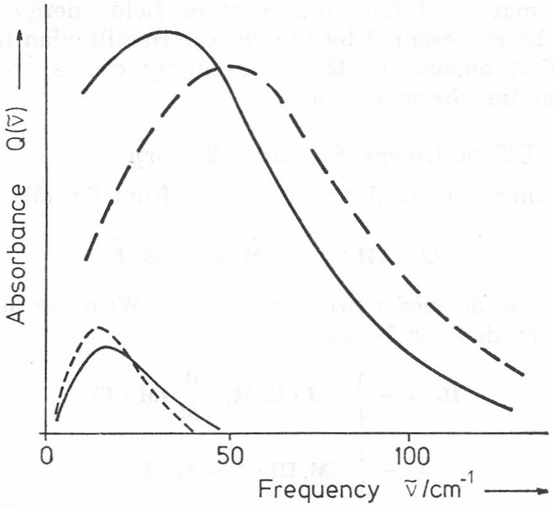
E_0: amplitude of the external electric wave.

Eq. (7) is *rigorous*, therefore, in the sense of linear response theory. It represents a generalization of the well known version of the FDT[16-17]

$$\underset{\text{old}}{Q(\omega)} \propto \frac{1}{\hbar} |E_0|^2 \tanh(\beta\hbar\omega/2) \cdot \omega \cdot \hat{C}(\omega) \tag{8}$$

The weakness of Eq. (8) will be shown in connection with some remarks concerning the theorem of minimum entropy production in the microscopic time scale (see Sec. 5 and Appendix A).

As an illustrative example of the importance of the generalized FDT the following experimental result can be mentioned:



Schematic representation of the temperature dependence of FIR absorption bands of acetonitrile in *n*-heptane; comparison with the gas-phase rotational spectrum of acetonitrile (lower left side).
Solid lines: T = 345 K; dashed lines T = 248 K. Cf. refs. 11, 14 and 25.

The FIR absorption spectra of acetonitrile in some solutions show an »anomalous« temperature dependence[14], see Figure. By increasing temperature the absorption bands of the solutions become narrowed. This seems to indicate an »anti-Boltzmann« behavior, as we see by comparison with the shape change of the corresponding gas spectrum.

This effect is anomalous only with respect to the usual FDT, Eq. (8); it plainly confirms the importance of the term with $\hat{C}'$, appearing in Eq. (7), cf. ref. 11.

3. THE AMOUNT OF ENERGY DISSIPATION

In the first paper[11] of this series we have already pointed out the inequality

$$\omega \cdot \hat{C}(\omega) \geqq \omega^{-1} \cdot \hat{C}'(\omega) \tag{9}$$

This relation follows directly from

(i) the form of the interaction Hamiltonian and the exact form of its time derivative,

(ii) the generalized FDT, i. e. (7), and

(iii) the Second Law of thermodynamics.

An important mathematical condition is the analyticity of the used after-effect functions in the lower complex halfplane including the real axis.

This relation, therefore, must be a fundamental inequality valid in several cases in molecular quantum-mechanical statistics, even though, of course, in some other cases the approximation

$$\omega \cdot \hat{C}(\omega) = \omega^{-1} \cdot \hat{C}'(\omega) \tag{9a}$$

is valid, which also means that $Q(\omega) = 0$.

3.1. *On the Memory Effects in the Short-time Behavior of the Dynamical Quantity* M

Eq. (9a) is usually obtained (in the case of an »one-sided« time correlation function) from

$$\begin{aligned}
\langle \dot{\mathbf{M}}(t_o) \cdot \dot{\mathbf{M}}(t_o + t)\rangle &= \frac{\partial}{\partial t} \langle \dot{\mathbf{M}}(t_o) \cdot \mathbf{M}(t_o + t)\rangle \\
&= \frac{\partial}{\partial t} \langle \dot{\mathbf{M}}(t_o - t) \cdot \mathbf{M}(t_o)\rangle \\
&= - \frac{\partial^2}{\partial^2 t} \langle \mathbf{M}(t_o - t) \cdot \mathbf{M}(t_o)\rangle \\
&= - \frac{\partial^2}{\partial^2 t} \langle \mathbf{M}(t_o) \cdot \mathbf{M}(t_o + t)\rangle
\end{aligned} \tag{10}$$

and the Fourier transformation of this result, see e. g. ref. 29.

This derivation, however, makes use of some very restrictive conditions, since generally the dynamical equation

$$\dot{\mathbf{M}} \equiv \frac{d}{dt} \mathbf{M} = \frac{1}{i\hbar} [\mathbf{M}, \mathbf{H}] + \frac{\partial}{\partial t} \mathbf{M}$$

is valid[30].

Derivation (10) makes sense if $[\mathbf{M}, \mathbf{H}] = 0$.

Nevertheless, (10) is correct in the special case of a *macroscopic* quantity, e. g. magnetization of a NMR-probe.

For this case van Kampen has already shown that the above commutator can be neglected to a very good approximation[13-33]. This result has been confirmed by van Vliet, too (cf. 21 Sec. 9.3). A second proof of (9a) can be given for the Markovian case[28]

$$\dot{\mathbf{M}} = \frac{1}{i\hbar}[\mathbf{M}, \mathbf{H}] \tag{11}$$

The straightforward proof makes use of the cyclic permutivity of the trace and the assumption that $\mathbf{H}$ *commutes with* ϱ.

$$\frac{d^2}{dt^2}\langle \mathbf{M}(O) \cdot \mathbf{M}(t)\rangle = \left(\frac{1}{i\hbar}\right)^2 \mathrm{Tr}\varrho\mathbf{M}(O)\,[[\mathbf{M}, \mathbf{H}], \mathbf{H}]$$
$$= \ldots = -\langle \mathbf{M}(O) \cdot \mathbf{M}(t)\rangle \tag{12}$$

As in the derivation of Eq. (10) here again it has been presupposed that *stationarity* holds and, additionally, that ϱ is a *static* quantity; these conditions will be treated in the following sections. Of course, Eq. (11) physically means that the system under consideration (with Hamiltonian $\mathbf{H}$) must be *isolated.* But this case is of less interest (see Sec. 1.2). Nevertheless, both derivations are valid to a certain extent. As a result, van Vliet's statement on vanishing dissipation in Kubo's LRT is confirmed in these cases (cf. Sec. 1.2 and ref. 25.).

From the derivations (10) and (12) we see that the following statement holds:

Statement I: The equation (9a) is valid *only* if the (formal) operator $\mathrm{Tr}\,(\varrho \cdots)$ commutes with d/dt and $\int dt$) and the condition of stationarity holds.

But the named operators generally do not commute. This can be shown with the aid of Mori's generalized Langevin equation [34] concerning the quantum-mechanical operator $\mathbf{M}(t)$

$$\frac{d}{dt}\mathbf{M}(t) = -\int_0^t \varphi(t-s) \cdot \mathbf{M}(s)\,ds + \mathbf{f}(t) \tag{13}$$

Now let us assume the general validity of the commutation mentioned above, and as a consequence we will derive a *contradiction.* (The following derivation is shortened; a rigorous treatment can be found in Ref. 25).

A formal multiplication of Eq. (13) with $\mathrm{Tr}\,\varrho\,\mathbf{M}(t_o)$ and interchanging the order of the named operators yield

$$\frac{d}{dt}\langle \mathbf{M}(t_o) \cdot \mathbf{M}(t)\rangle = -\int_0^t \varphi(t-s) \cdot \langle \mathbf{M}(t_o) \cdot \mathbf{M}(s)\rangle\,ds + \langle \mathbf{M}(t_o)\,\mathbf{f}(t)\rangle \tag{14}$$

The second term on the right is usually equal to zero due to the fact that in many cases $\mathbf{f}(t)$ fluctuates very fastly (compared with the »fluctuation time« of $\mathbf{M}(t)$). Therefore, in the limit $t_o \to t$ it follows

$$\frac{d}{dt}\langle \mathbf{M}(t)^2\rangle \overset{?}{\doteq} -\int_0^t \varphi(t-s)\,\langle \mathbf{M}(t) \cdot \mathbf{M}(s)\rangle\,ds \tag{15}$$

As is known, the left-hand side is always zero. On the other hand, the right-hand side generally does not vanish and this is a *contradiction* concerning (9a) and (10) as well. (This method of proof has a *formal* similarity to the one used by Zwanzig in ref. 28 p. 2530.). Thus, even the second statement holds[25]:

Statement IIa: The operator $Tr\,(\varrho \cdots)$ generally *does not* commute with d/dt or $\int dt$.

This result can also be formulated in more physical terms:

Statement IIb: The equation (9a) is generally wrong if the dynamical quantity $\mathbf{M}$ shows a *non-Markovian* behavior and if $t < \tau_M$.

But it can be shown, of course, that Eq. (9a) is valid within the limit $t \gg \tau_M$[25,35].

3.2. *On the Neglect of Time-odd Variables by the Long-time Treatment of a »Markovian« System*

An observable can quite generally be classified as time-even or time-odd depending on whether they do or do not change sign under the time reversal transformation. In a nomenclature introduced by Casimir[36] and also used by de Groot and Mazur[35] the time-even and time-odd variables are called *α-variables* and *β-variables,* respectively. (Here the symbol β is not to be confused with quantity $1/kT$.)

Now it is important to note that Eq. (9a) also lacks general validity within the »standard« theory of irreversible processes[35]. Here the dynamical behavior of $\mathbf{M}(t)$ is assumed to be *Markovian.* Equation (9a) is only valid if some restrictive conditions are met (see ref. 35. Sec. VII§4 and VIII§2):

(i) Each dynamical β-variable (i. e. in our case $\dot{\mathbf{M}}$) must be uniquely *definable* through an appropriate α-variable (i. e. M).

(ii) The β-variables must not be needed for the dynamical description of the system.

(iii) The decay time of a fluctuation of a β-variable must be much smaller than the decay time of a fluctuation of the corresponding α-variable.

Consequently, Eq. (9a) holds only in the »long-time« limit. These conditions, of course, depend on each other. (iii) is a common condition if one deals with macroscopic variables[8,28,35].

(i) and (ii) are physically very restrictive, because they imply that only a *subset of the whole phase space is sufficient for the statistical-mechanical treatment of the system.* From this also follows that the α-variable is a *coarse grained* variable. It must be pointed out that variables of this kind are of no interest for the description of the microscopic dynamical behavior of matter dealt with. As a result the following statement holds:

Statement IIc: The equation (9a) is wrong in the »short-time« limit even if the system shows a Markovian behavior[25].

In addition, the following remark should be pointed out: The derivation of the generalized FDT, Eq. (7), *does not make use* of the commutation forbidden by the statement IIa.

The main result of ref. 11. and of this paper can be reformulated, with the nomenclature used in this section, by the following: The FDT must be amended when the autocorrelation function of a β-variable such as $\dot{\mathbf{M}}$ is not equal to minus the second order time derivative of that of the corresponding α-variable, such as $\dot{\mathbf{M}}$.

3.3. *Fluctuations Concerning the Ensemble Statistical Operator ϱ of a Spectroscopic System*

The existence of many degrees of freedom in a physical system automatically implies *spontaneous* fluctuations; we can say that they have an »internal« origin. On the other hand, a system can also show fluctuations with an »external« origin, e. g. from a temporary disturbance of the boundary conditions[20,35–40]. These facts also can provide an illustration for the formal statement IIa.

3.3.1. *Fluctuations Due to Coupling of the System with the Environment*

Van Vliet has recently shown how to generalize the linear response formalism for the treatment of systems which are coupled with a thermal reservoir[21–22], see also ref. 25. This coupling can be represented explicitly by van Vliet's partitioning of the system Hamiltonian

$$\mathbf{H}_o \rightarrow \mathbf{H}_o + \lambda \mathbf{V}, \qquad \lambda = \text{const.} \tag{16}$$

$\mathbf{H}_o$ on the right is a functional of the coordinates and momenta of the particles constituting the system, whereas $\lambda \cdot \mathbf{V}$ depends on the coordinates and momenta of both the system and the heat bath. Therefore, the »exact« statistical operator[21]

$$\varrho_{\text{micr}} \overset{\text{def}}{=} \frac{1}{Z} \cdot \exp \beta \cdot (-\mathbf{H}_o - \lambda \mathbf{V}) \tag{17}$$

must be »projected« onto the phase-space area concerning the physical system under consideration. (This can be carried out e. g. by Zwanzig's method[41–42]). Such a »projection« usually implies an explicit time dependence for ϱ, as we can see from the following:

In an approximation we get the statistical operator ϱ by

$$\varrho = Tr^{(\text{bath})}\, \varrho_{\text{micr}} \tag{18}$$

i. e. if an adiabatic approximation for the bath degrees of freedom would be valid[21]. By means of this procedure the operator ϱ in general becomes explicitly time dependent due to the fact that the operator $Tr^{(\text{bath})}$ depends on the time during which the trace formation has been carried out. Therefore, for a »small« coupling $\lambda \cdot \mathbf{V}$ the statistical operator attains the form

$$\varrho(t) = \varrho_{\text{eq}} + \lambda \cdot \Delta^{(\text{bath})} \varrho(t) \tag{19}$$

with

$$\varrho_{\text{eq}} = \frac{1}{Z'} \cdot \exp(-\beta \mathbf{H}_o) \tag{20}$$

Note that the von Neumann equation generally does not hold for ϱ, if $\lambda \mathbf{V}$ is neglected:

$$\frac{\partial}{\partial t} \varrho \neq \frac{1}{i\hbar} [\mathbf{H}_o, \varrho] \tag{21}$$

Additionally it is important to note that the »exact« density operator, Eq. (17), cannot commute with $\mathbf{H}_0$ for all times; it follows that the use of ϱ_{eq}, which commutes with $\mathbf{H}_0$ for all times, introduces a repeated random phase assumption into the calculations, ref. 43 p. 1205. This has already been mentioned in Sec. 1.2.

3.3.2. *Spontaneous Fluctuations and the Stationarity Condition*

As mentioned above, these kind of fluctuations does not have a deterministic mechanical origin. For our purposes, we can formulate the *ansatz*

$$\varrho(t) = \varrho_{eq} + \Delta^{(sp)}\varrho(t) \tag{22}$$

where the second term on the right-hand side is explicitely time dependent. For this statistical operator, too, relation (21) holds. The stationarity condition, therefore, as mentioned in statement I., cannot hold in the short-time limit of observation. (This result is valid very generally in quantum mechanics, see ref. 20 § 5, since the relation $\varrho = \varrho_{eq}$ becomes incorrect in this time limit.).

3.3.3. *Consequences for Spectroscopic Systems*

We consider a spectroscopic probe consisting of a dilute solution of dipolar molecules in a nonpolar solvent. We can regard a few dipolar molecules with the surrounding molecules of the solvent as being a »system«. In this case the heat bath for each system consists of the remaining part of the probe. Thus we see that van Vliet's ansatz (21) finds a natural interpretation:

The coupling operator $\lambda \cdot \mathbf{V}$ *represents the interaction between the systems,* e. g. by contact of their surfaces and/or by dipole-dipole interaction etc.

The fact that the whole spectroscopic probe has many degrees of freedom implies the existence of spontaneous fluctuations concerning the ensemble density operator ϱ.

These remarks also permit an illustrative interpretation of the statement IIa in the following way:

We consider the time derivative of the ensemble average $Tr\,\varrho\mathbf{X}$, where $\mathbf{X}$ is an arbitrary operator representing an observable quantity,

$$\frac{d}{dt} Tr\,\varrho \cdot \mathbf{X} = Tr\,\varrho\,\dot{\mathbf{X}} + Tr\,\dot{\varrho}\,\mathbf{X} \tag{23}$$

With the formal ansatz $\varrho(t) = \varrho_{eq} + \delta\varrho(t)$, see (19) and (22), and the obvious relation

$$Tr\,\varrho_{eq}\,\dot{\mathbf{X}} \gg Tr\,\delta\,\varrho(t)\,\dot{\mathbf{X}} \tag{24}$$

we obtain

$$\frac{d}{dt} Tr\,\varrho\,\mathbf{X} \cong Tr\,\varrho_{eq}\,\dot{\mathbf{X}} + Tr\,(\frac{d}{dt}\,\delta\,\varrho(t))\cdot\mathbf{X} \tag{25}$$

The first term on the right represents the usual approximation in Kubo's linear response theory as it stands[1-2]. The second term is of importance, if the »relaxation« time of a *microscopic* quantity $\mathbf{X}$ is of the *same order of magni-*

tude as a characteristic fluctuation (or decay) time of the small term $\delta\varrho(t)$. Then we must regard the second term on the right of Eq. (25) to be of importance, which is due to the fact that the relation

$$Tr\,(\frac{d}{dt}\,\delta\,\varrho\,(t))\cdot\mathbf{X} \gg Tr\delta\,\varrho\,(t)\cdot\mathbf{X} \tag{26}$$

can be valid, if the term $\delta\varrho\,(t)$ fluctuates very quickly.

As a matter of fact, the time dependent term in Eqs. (19) and (22) fluctuates during a characteristic time of microscopic order of magnitude. Therefore, in the case of a *macroscopic* quantity **X** Eq. (25) can be replaced by

$$\frac{d}{dt}\,Tr\,\varrho\cdot\mathbf{X} \cong Tr\,\varrho_{eq}\,\mathbf{X} \tag{27}$$

as is usual in linear response theory.

We summarize:

If the coupling operator **M** in Eq. (2) represents a microscopic dynamical quantity of the system, we must take into account the fluctuations concerning the density operator ϱ of the ensemble. Namely both **M** and ϱ can »fluctuate« with characteristic times of a comparable order of magnitude and, therefore, we must be careful when performing the time derivation of an ensemble average. Thus, Eq. (25) shows that these fluctuations imply the non-commutation of the operators d/dt and $Tr\,(\varrho\cdots)$.

4. ON THE DOMAINS OF APPLICATION FOR THE GENERALIZED FDT

As can be seen from the statements put forward in chapters 2. and 3., this question is to be answered by the detailed analysis of the quantities constituting the interaction operator $\mathbf{H}_I$. The form (1) of the interaction operator

$$\mathbf{H}_I = -\mathbf{M}\cdot\mathbf{E}$$

proves that the generalization (7) is important for those cases where the »characteristical times« of the dynamic behavior of the quantities **M** and **E** are of *comparable* magnitude.

The range of application of the named theorem may also include

i) parts of the vibrational-rotational spectroscopy of the middle IR in the liquid or compressed gas phase,
ii) the corresponding experiments with molecules being adsorbed on surfaces,
iii) parts of the corresponding Raman spectroscopy,
iv) depolarized light (Rayleigh) scattering experiments.

The named range of application does certainly *not* include

i) those cases where **M** is a bulk matter quantity and **E** an external disturbance of (relatively) slow frequency,
ii) UV spectroscopic experiments in the liquid phase, since the electronic transitions and the corresponding external disturbance are much »faster« than the reorientation-vibration processes of the molecules considered. (Those are only to be observed by means of the decay functions of the degree of fluorescence polarization of e. g. aromatic compounds in dilute solutions[44].)

5. IS THE THEOREM OF MINIMUM ENTROPY PRODUCTION (TMEP) VALID ON THE MICROSCOPIC TIME SCALE?

This well-known theorem[45,35,37] states that if a steady state of a system occurs sufficiently close to an equilibrium state, it may be characterized by an extremal principle according to which the *entropy production* P has its minimum value at the steady state compatible with the prescribed special constraints.

The TMEP has been proved within the framework of *phenomenological* theory[35,37] and, to our knowledge, it has no analogue within Kubo's statistical-mechanical theory of irreversible processes. Therefore, it is surprising to note that the generalized FDT Eq. (7) seems to have close reference to the TMEP, at least in some interesting limited cases. This will be treated in the following section especially with regard to a spectroscopic experiment.

Firstly we define the entropy production P within the framework of Kubo's theory of irreversible processes by

$$P(\omega) \overset{\text{def}}{=} \frac{Q(\omega)}{T} \tag{28}$$

T is the temperature of the heat bath; the ensemble is canonical. This definition is physically meaningful due to the fact that the coupling of the system with the external field, Eq. (1), is very weak and, therefore, the ensemble remains in thermal equilibrium.[1,2] The term $P(\omega)$ still represents, of course, a microscopic quantity. In a spectroscopic experiment one rather observes the quantity

$$\overset{\text{macro}}{P}(\omega) = \sum_{i=1}^{N} P_i(\omega) \equiv \sum_{i=1}^{N} Q_i(\omega)/T \tag{29}$$

N is the number of microscopic systems constituting the material probe. The subscript i expresses the assignment of the quantities P and Q to the i-th system of the ensemble. (For simplicity, for the absorption cross-section holds $\sigma = 1$).

Usually a spectroscopic experiment with a *weak* irradiation source (i. e. no laser!) takes time of a macroscopic order of the magnitude. The fluctuation phenomena mentioned in Sec. 3, therefore, have the same time-average effect on each one of the members of the ensemble. Therefore it holds

$$\overset{\text{macro}}{P}(\omega) \cong N \cdot P(\omega) = N \cdot \frac{Q(\omega)}{T} \tag{30}$$

As a realistic example we now consider a very low pressure gas of dipolar molecules, which constitute the ensemble of interest. Within a sufficiently short time interval Δt, the system can be regarded as an ensemble of *isolated* particles. Δt must be very much shorter than the mean »free flight time« of a molecule.

In this case, however, the spectroscopic probe can *absorbe* irradiation energy but *cannot dissipate* it *during* Δt; this is due to the fact that entities like heat, temperature and entropy have no physical meaning within the framework of the »one-body-problem«. In the case under consideration, therefore, the entropy production must be equal to zero.

This result can also be formally achieved with Eq. (30) and the generalized FDT by means of the following steps:

i) For each isolated particle the equation of motion (11) holds.
ii) We regard the ensemble to be stationary, and in thermal equilibrium with non-fluctuating density operator ϱ_{eq}.
iii) The derivation (12) now holds.

Thus, $Q(\omega) = 0$, *q. e. d.* In this case the entropy production reaches its absolute minimum, namely it vanishes!

These considerations can also be applied to the interaction of an ideal crystal at very low temperature with a weak radiation field: Some excited states (e. g. optical phonons) can be created by absorption of radiation. This *absorption* process can be very fast compared with the time needed for the *dissipation* of the energy contained in these quasi-particles. This is due to the fact that dissipation (i. e. the decay of these states) is caused by »scattering« processes between these quanta.

In another case the quantity **M** will be *macroscopic,* e. g. the magnetization of an NMR probe. The »short-time« dynamical behavior, i. e. $t \ll \tau_M$, is then given by

$$\frac{d}{dt}\mathbf{M} = \frac{1}{i\hbar}[\mathbf{M}, \mathbf{H}_o] + \frac{\partial}{\partial t}\mathbf{M}(t) \tag{31}$$

As van Kampen has already shown (see Sec. 3.1),

$$[\mathbf{M}, \mathbf{H}_o] \approx 0$$

Thus, Eq. (31) degenerates to the form

$$\frac{d}{dt}\mathbf{M} = \frac{\partial}{\partial t}\mathbf{M}$$

and, therefore, derivation (10) yields the desired result

$$Q(\omega) = 0, \quad \text{if} \quad t \ll \tau_M \tag{32}$$

Of course, this is physically meaningful, since within this time limit the system can be considered as conserved.

We summarize:

The validity of the TMEP on the considered molecular level can be shown in some »trivial« cases, where $Q(\omega)$ vanishes.

A general proof of this theorem within the framework of Kubo's microscopic-statistical theory of irreversible processes should use a concrete interrelation between the time autocorrelation functions C and C', which does not seem to exist yet.

Further relations between the generalized FDT and the TMEP will be published soon.

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APPENDIX A

A Molecular-Mechanical Model to Illustrate the FDT

It is certainly instructive to illustrate the generalized FDT, Eq. (7), and the »old« version, Eq. (8), by means of a classical-mechanical analogue.

For this purpose, we first derive the »classical« limit of these relations, i. e. $\hbar \to 0$. Then from the well-known approximation (8) follows:

$$Q_{\text{old}}(\omega) \propto E_o^2 \cdot \beta \cdot \omega^2 \cdot \hat{C}(\omega) \tag{A1}$$

which is simply the Fourier transform of the following equation:

$$Q_{\text{old}}(t) \propto E_o^2 \cdot \beta \cdot \{-\frac{\partial^2}{\partial t^2} C(t)\} \tag{A1a}$$

In the same way from the generalized FDT, Eq. (7) follows

$$Q(\omega) \propto E_o^2 \cdot \beta \cdot \{\omega^2 \cdot \hat{C}(\omega) - \hat{C}'(\omega)\} \tag{A2}$$

and by Fourier transformation

$$Q(t) \propto E_o^2 \cdot \beta \cdot \{-\frac{\partial^2}{\partial t^2} C(t) - C'(t)\} \tag{A2a}$$

where $C(t) = \langle M(O) \cdot M(t)\rangle$ and $C'(t) = \langle \dot{M}(O) \cdot \dot{M}(t)\rangle$
In the classical limit the products appearing in the correlation functions do not need to be symmetrized.

As an example we consider a quantity of molecules with permanent electrical dipole moment $\vec{M}$ being dissolved in a nonpolar solvent. Then $M(t)$ and $\dot{M}(t)$ in the relations (A1a) and (A2a), respectively, are the projections of $\vec{M}(t)$ and $\dot{\vec{M}}(t)$, respectively, onto the space axis marked out by the external field $\vec{E}$.

At first we can formally assign a fictitious »mass point« with the »space coordinate« $M(t)$, the »speed coordinate« $\dot{M}(t)$ and the »mass« μ to each molecule. μ will be a function of the molecular momentum of inertia. With it the molecular reorientational motion is described by the one-dimensional motion of a »point«.

After this we will consider the relations (A1a) and (A2a) only within »small« time intervals Δt, so that

$$M(t_o) \cong M(t_o + t),\ \dot{M}(t_o) \cong \dot{M}(t_o + t),\ \ddot{M}(t_o) \cong \ddot{M}(t_o + t) \tag{A3}$$

$$\text{in the time interval } |t - t_o| < \Delta t$$

will be valid for all fictitious points.

The starting point for our mechanical example is represented by the following *Newtonian* dynamical equation:

$$\mu \cdot \ddot{M}(t) = -\frac{\partial U}{\partial M}\bigg|_t - r \cdot \dot{M}(t) \tag{A4}$$

which will be assumed to describe the motion of the fictive point during the time interval $t_o < t < t_o + \Delta t$. The first term on the right-hand side represents the *conservative* force component, whereas the second term describes a *dissipative* component, e. g. friction[46].

We multiply Eq. (A4) from the left by $M(t)$ and obtain

$$\mu M(t) \cdot \ddot{M}(t) = -M(t) \cdot \frac{\partial U}{\partial M} - M(t) \cdot r\dot{M}(t) \tag{A5}$$

The potential U can be considered as being *harmonic,* because of the following reason: If the solvent is thought to be »frozen« U describes the »potential well« containing the fictitious point under consideration. As usual, in the first approximation this point accomplishes a harmonic oscillation during the preassumed short time interval Δt. Therefore, it holds $2U = \frac{\partial U}{\partial M} \cdot M$, and Eq. (A5) yields

$$\mu \cdot M(t) \cdot \ddot{M}(t) = -2\,U - M(t) \cdot r\dot{M}(t) \tag{A6}$$

We like to compare this result with the »classical limit« (A1a) of the incomplete FDT. Using the approximation

$$\frac{\partial^2}{\partial t^2}\, C(t) = \langle M(0) \cdot \ddot{M}(t) \rangle,$$

(see Sec. 3) we obtain from (A1a)

$$Q_{\text{old}}(t) \propto E_o^2 \cdot \beta \cdot \{-\langle M(0) \cdot \ddot{M}(t) \rangle\} \tag{A7}$$

With the approximation (A3) and with the stationarity condition for the time correlation functions we obtain from (A7) by multiplication with μ

$$Q_{\text{old}}(t) \propto E_o^2 \cdot \beta \{-\langle \mu M(t) \cdot \ddot{M}(t) \rangle\} \tag{A8}$$

The right-hand side can be further evaluated with the aid of the classical-mechanical expression (A6) and its ensemble average. Thus from (A6) and (A8) follows

$$Q_{\text{old}}(t) \propto E_o^2 \cdot \beta \cdot \{2\,\langle U \rangle + \langle M(t) \cdot r\dot{M}(t) \rangle\} \tag{A9}$$

Now we realize an essential weakness of the usual incomplete version (8) of the FDT: In connection with our example Eq. (A4) a *non-vanishing dissipation* $Q_{\text{old}}(t)$ is predicted even if *no dissipative forces* are acting on the system! This absurd result follows from relation (A9) by setting the friction force equal to zero, i. e. $r = 0$. Obviously something is wrong.

Now we will derive the analogous result from the generalized FDT (7) and its classical limit (A2a).

A multiplication of relation (A2a) with μ and the approximation (A3) yield

$$Q(t) \propto E_o^2 \cdot \beta \cdot \{-\langle \mu M(t) \cdot \ddot{M}(t) \rangle - \langle \mu \dot{M}(t)\ \dot{M}(t) \rangle\} \tag{A10}$$

The first term on the right-hand side was calculated above, see relation (A8). The second term represents twice the ensemble average of the »kinetic energy« T of one of our fictive points,

$$\langle \mu \dot{M}(t) \cdot \dot{M}(t) \rangle = 2\,\langle T \rangle.$$

Based upon the Virial theorem for the dynamic process (A6) it holds for ergodic ensembles $\langle U \rangle = \langle T \rangle$[46] and thus

$$Q(t) \infty E_o^2 \cdot \beta \cdot \{2\,\langle U \rangle + \langle M(t) \cdot r\dot{M}(t) \rangle - 2\,\langle T \rangle\} \equiv E_o^2 \cdot \beta \cdot \langle M(t) \cdot r\dot{M}(t) \rangle$$

The correlation function on the right-hand side does not vanish; this is due to the fact that the friction coefficient r shows the same behavior under time reversal as the quantity $\dot{M}$; see Eq. (A4). Now we obtain the assumed result: In the special case of *no dissipation forces* acting on the system, the *dissipation* $Q(t)$ *vanishes.*

This result is physically meaningful.

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IZVLEČEK

Statistični opis dinamičnih procesov molekul v tekočinah. Uporaba absorpcijske spektroskopije v daljnem infrardečem območju

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Z absorpcijsko spektroskopijo v daljnjem infrardečem področju (FIR-far IR), se da zelo uspešno zasledovati dinamiko molekulskega gibanja v raztopinah in kondenziranih plinih v okviru teorije linearnega odziva (linear response theory LRT), ki jo je vpeljal Kubo. Dinamiko molekule opazujemo posredno preko njenega permanentnega dipolnega momenta $\vec{M}$, ki je v primeru, ko se molekula nahaja v zunanjem elektromagnenem polju, sklopljen s njim, kar popiše semiklasični interakcijski Hamiltonian.

Članek obravnava fizikalno zasnovo, izpeljavo in veljavnost posplošenega fluktuacijsko-disipacijskega teorema (FDT), ki je v zadnjem času znatno prispeval k statistični mehaniki neravnotežnih stanj.

Pokazano je, da so za disipacijo iradijacije odgovorni: kratkoživost operatorja, ki sklaplja sistem z iradiacijskim poljem, spontane fluktuacije, ki jih kaže statistični operator v mikroskopski časovni skali in vpeljava sklopitve sistema s termično kopeljo v formalizmu Kubove teorije, ki jo je predpostavil van Vliet.

Posledica tega je časovna odvisnost statističnega operatorja na kratkočasovni skali.

Posplošen FDT pa predstavlja v okviru mikroskopske Kubove teorije mikroskopsko interpretacijo. Prigoginovega teorema v minimalni tvorbi entropije (CTMEP).

Teorija je pripravna za interpretacijo rezultatov, ki jih dobimo iz: vibracijsko-rotacijskih spektrov v srednjem infrardečem področju in to tekočin ali kondenziranih plinov, spektrov adsorbiranih molekul na površinah, dela Ramanskih spektrov in eksperimentov z Rayleighovim sipanjem, ni pa ustrezna v primeru, ko je dipolni moment $\vec{M}$ makroskopska količina, iradiacijsko polje pa ima visoko frekvenco in v primeru UV spektroskopije, ko so elektronski prehodi dosti bolj kratkoživi, kot so ustrezni vibracijsko-orientacijski procesi molekul v raztopinah in kondenziranih plinih.