A Note on the Off-Diagonal Elements of the Density Matrix in Thermal Equilibrium and Thermal Radiation

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A closer look at the off-diagonal elements of the density matrix of a thermal gas phase molecular ensemble reveals, that they lead to a contribution to thermal radiation which increases in power proportional to the number of particles. A quantitative comparison of this contribution to the one originating from spontaneous emission is given.

In treatments of relaxation processes in gas phase spectroscopy the off-diagonal elements of the density matrix are usually set to zero in thermal equilibrium [1]. To justify this approximation the following argument is used: "Due to collisions the phases, φ_ν, of the contributions of the individual molecules will be statistically spread and if the ensemble comprises a sufficiently large number of particles, N, the sum

$$\frac{1}{N}\sum_{\nu=1}^{N} e^{i\varphi_\nu}$$

may be approximated by the integral

$$\frac{1}{2\pi}\int_0^{2\pi} e^{i\varphi}\,\mathrm{d}\varphi$$

which is zero". However, since one is usually interested to calculate most probable values for macroscopic observables, for instance the polarization of a sample, the factor $1/N$, present in the expression for the density matrix elements, is compensated by another factor of N (see below) and the basic problem is essentially that of calculating the most probable absolute value of the sum $\sum_{\nu=1}^{N} e^{i\varphi_\nu}$. With increasing N this value is known to go to infinity proportional to $\sqrt{N}$ rather than to zero. Thus it is not immediately obvious that contributions due to off-diagonal elements may indeed be neglected in thermal equilibrium and a more detailed look at the problem which is closely related to the random walk problem or to diffusion in a plane is presented in the following.

For the convenience of the reader I will first briefly recall some basics of the density matrix formalism used to treat emission and absorption in gasphase samples. Assume an ensemble of non-interacting identical molecules. Further assume the complete set of eigenfunctions of the unperturbed Hamiltonian of the individual molecule to be known: $\psi_m(q)$ $(m = 1, 2, \ldots)$. Then the state function for an individual molecule, for instance for the ν-th molecule, may be expanded with respect to this basis set with time dependent coefficients $a_m^{(\nu)}(t)$:

$$\Psi^{(\nu)}_{(q,t)} = \sum_{m}^{\text{eigenstates}} a_m^{(\nu)}(t)\cdot\psi_m(q)\,,\qquad \nu = 1,\,2,\,\ldots,\,N \qquad (1)$$

with

$a_m^{(\nu)}(t) = a_m^{(\nu)}(t_\mathrm{c})\cdot\exp\left\{-\frac{i}{\hbar}E_m(t-t_\mathrm{c})\right\}$ (from the time dependent Schrödinger equation),

E_m = m-th eigenvalue of the unperturbed Hamiltonian,

t_c = time at which the molecule experienced its last collision,

$a_m^{(\nu)}(t_\mathrm{c})$ = coefficient of the m-th basis function with which the molecule emerged from its last collision.

Since rotational energy spacings are usually small with respect to kT, there is no obvious reason that the molecules should emerge in eigenstates of the unperturbed Hamiltonian. I rather assume that the molecules emerge in mixed states, each with a time dependent probability density and thus emitting (incoherent) radiation.

With state functions according to Eq. (1), the ensemble average of the expectation value of any one-particle operator, say for instance $\hat\mu_z$, the component of the electric dipole moment in direction of the space fixed Z-axis, takes the following form:

$$\overline{\langle\hat\mu_z\rangle} = \frac{1}{N}\sum_{\nu=1}^{N}\sum_{m}\sum_{n} a_m^{(\nu)*}(t)\,a_n^{(\nu)}(t)\,\mu_{zm,n} \qquad (2)$$

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with

$$\mu_{zm,n} = \langle \psi_m | \hat{\mu}_z | \psi_n \rangle .$$

Equation (2), the expression for the average single particle expectation value of $\hat{\mu}_z$, may be rewritten as:

$$\overline{\langle \hat{\mu}_z \rangle} = \sum_m \sum_n \varrho_{nm} \cdot \mu_{zm,n} = \frac{1}{N}\, \mu_{\text{macro}} \tag{3}$$

with

$$\varrho_{n,m} = \frac{1}{N} \sum_{\nu=1}^{N} a_m^{(\nu)*}(t)\, a_n^{(\nu)}(t) , \tag{4}$$

the n,m-element of the density matrix, referred to the complete set of eigenfunctions of the unperturbed Hamiltonian and $\mu_{\text{macro}} \mathrel{\hat{=}}$ the macroscopic dipole moment exhibited by the ensemble. As mentioned in the introduction, it is the aim of this note to give a reasonable estimate for the absolute values of the off-diagonal elements $|\varrho_{m,n}|$ $(m \neq n)$.

With no neglect in generality we may first write:

$$a_m^{(\nu)}(t) = |a_m^{(\nu)}| \exp\{i\, \varphi_m^{(\nu)}\} \exp\left\{-\frac{i}{\hbar}\, E_m t\right\} \tag{5}$$

with $\varphi_m^{(\nu)}$ a random phase, which depends on the random phase with which the molecule emerged from its last collision.

From Eq. (5) the expression for the off-diagonal element $\varrho_{m,n}$ takes the following form

$$\begin{aligned} \varrho_{m,n} = \frac{1}{N} \Bigg\{ & \sum_{\nu=1}^{N} |a_m^{(\nu)}| \cdot |a_n^{(\nu)}| \cdot \exp\{i(\varphi_m^{(\nu)} - \varphi_n^{(\nu)})\} \\ & \cdot \exp\left\{-\frac{i}{\hbar}(E_m - E_n)\, t\right\}\Bigg\}. \end{aligned} \tag{6}$$

We will now have a more detailled look at the sum enclosed in the wavy brackets.

From a comparison of the diagonal elements of the intensity matrix with Boltzmann statistics:

$$\varrho_{mm} = \frac{1}{N} \sum_{\nu=1}^{N} |a_m^{(\nu)}|^2 = \frac{\exp\{-E_m/k\,T\}}{Z} \tag{7}$$

($Z = \sum_l \exp\{E_l/k\ T\}$ the partition function) one may first get an estimate for the average absolute value of the coefficients $|a_m^{(\nu)}|$ as:

$$\overline{|a_m^{(\nu)}|} = \sqrt{\exp\{-E_m/k\,T\}/Z} . \tag{8}$$

With this estimate we may then rewrite the sum in Eq. (6) as given in (9):

$$\{\ \} \cong \sum_{\nu=1}^{N} \frac{\exp\left\{-\left(\dfrac{E_m + E_n}{2\,k\,T}\right)\right\}}{Z} \cdot \exp\{i(\varphi_m^{(\nu)} - \varphi_n^{(\nu)})\} . \tag{9}$$

The evaluation of the most probable absolute value for this sum, let us call it A, is equivalent to solve the random flight problem in two dimensions with a constant length,

$$L = \exp\left(-\frac{E_m + E_n}{2\,k\,T}\right) \Big/ Z ,$$

between two successive changes in direction.

The solution is [2]:

$$A = \frac{2}{\pi}\, L \sqrt{N} = \frac{2}{\pi}\, \frac{\exp\left\{-\left(\dfrac{E_m + E_n}{2 \cdot k\,T}\right)\right\} \sqrt{N}}{Z} \tag{10}$$

which goes to infinity with increasing N rather than to zero as suggested by the standard argument mentioned in the introduction. As a result from Eq. (10) together with Eqs. (3) and (6), the ensemble will exhibit a nonzero time dependent macroscopic dipole moment. Of the many (incoherent) contributions let us pick the one which oscillates with frequency $\omega_{mn} = (E_m - E_n)/\hbar$. From (3), (6), and (10) its most probable amplitude may be estimated as

$$\mu_{\omega_{mn}} = \sqrt{N}\, \frac{2}{\pi}\, \frac{\exp\left\{-\left(\dfrac{E_m + E_n}{2 \cdot k\,T}\right)\right\} |\mu_{m,n}|}{Z} \tag{11}$$

which gives rise to an average radiated power, calculated from classical electrodynamics as [3]:

$$\begin{aligned} \bar{P}_{\omega_{m,n}} &= \frac{\omega_{m,n}^4}{3\,C^3}\, \mu_{\omega_{m,n}}^2 \\ &= N\, \frac{\omega_{m,n}^4}{3\,C^3}\, \frac{4}{\pi^2}\, \frac{\exp\left\{-\left(\dfrac{E_m + E_n}{k\,T}\right)\right\} |\mu_{m,n}|^2}{Z^2} . \end{aligned} \tag{12}$$

It is now interesting to compare this expression to the corresponding well known expression for the thermal radiation due to spontaneous emission [4]:

$$P^{\text{spont}}_{\omega_{m,n}} = N\, \frac{\omega_{m,n}^4}{3\,C^3}\, 4\, \frac{\exp\{-E_m/k\,T\}}{Z}\, |\mu_{m,n}|^2 \tag{13}$$

where E_m is the upper level.

From (12) and (13) we get

$$P_{\omega_{m,n}} = \frac{1}{\pi^2} \, \frac{\exp\{-E_n/k\,T\}}{Z} \, P^{\text{spont}}_{m,n} \, .$$

where E_n is the lower level. With $\exp(-E_n/k\,T) \ll Z$, (Z includes the rotational partition function), the collisionally produced contribution to the incoherent radiation emerging from the ensemble — even though increasing in power proportional to N — is small as compared to the thermal radiation due to spontaneous emission and thus may indeed be safely neglected as long as the latter is negligible.

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[1] In this context authors typically quote Chapter 83 in R. C. Tolman's famous book: The Principles of Statistical Mechanics, Oxford University Press, Amen House, London E.C.4 (1-st ed. 1938), or directly refer to the "hypothesis of random phases" i.e. the argument presented in the introductory section of this note.

[2] see for instance: Charles Tanford, Physical Chemistry of Macromolecules, John Wiley & Sons, Inc., New York 1961, Chapter III, 10a.

[3] see for instance G. Joos, Lehrbuch der Theoretischen Physik, 12-th edition, Akademische Verlagsgesellschaft, Wiesbaden (1977), Chapter VII, 5.

[4] see for instance W. Döring; Einführung in die Quantenmechanik, Vandenhoek & Ruprecht, Göttingen 1955, Chapter II, 19.