YU ISSN 0015—3206
FZKAAA 16 (1) 23 (1984)

NONSTATIONARY PROCESSES AND ORDERING

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Received 14 September 1983

UDC 538.95

Original scientific paper

Nonstationary processes in two-component gaseous mixture are analysed. The life-times of pairs of particles, formed in nonstationary processes, were found. It was shown that only the pairs with parallel and antiparallel momenta have infinite life-times. After certain time all other pairs disappear. This effect is due to the dissipativity of nonstationary processes, and in this manner, the dissipativity pauses the ordering of the system.

1. Introduction

The molecular gaseous mixture will be analysed in this paper. In order to simplify calculations we shall consider the two-component mixture. It is assumed that molecules are in a chemical reaction and consequently, the number of initial particles is not conserved. In such a case the nonstationary processes can take place in the system. These processes can be analysed with help of nonstationary correlation functions which were introduced and analysed in many details in Ref. 1.

The kinetic energy of the whole system will be calculated, but the kinetic energies of particle pairs will be the object of our special attention. It will be shown that dissipativity, which is present in nonstationary processes, causes the ordering of the system.

2. *Time dependence of operators in two-component gaseous mixture*

We choose the model Hamiltonian of a two-component molecular mixture in the analytical form, analogous to that of three-level scheme exciton Hamiltonian[2,4,5]. The form of the model Hamiltonian is the following:

$$H = \sum_{ss'\vec{k}} X_{ss'}(\vec{k}) B_s^+(k) B_{s'}(\vec{k}) + \frac{1}{2} Y_{ss'}(\vec{k}) [B_s^+(\vec{k}) B_{s'}^+(-\vec{k}) + B_{s'}(-\vec{k}) B_s(\vec{k})]$$

$$s, s' \in (1,2). \tag{1.1}$$

The Bose-operators $B_s^+(\vec{k})$ and $B_s(\vec{k})$ in this Hamiltonian create and annihilate, respectively, a molecule of the mixture component s in the state with momentum $\hbar\vec{k}$. It is necessary to note that, strictly speaking, the operators creating and annihilating molecules in the given states do not obey boson kinematics, but they can be considered as bosons in the harmonical approximation used here[5].

The functions $X_{ss'}(\vec{k})$ and $Y_{ss'}(\vec{k})$ are defined as follows:

$$X_{ss'}(\vec{k}) = \Delta_s \delta_{ss'} + x_{ss'}(\vec{k}); \quad x_{ss'}(\vec{k}) = \frac{\hbar^2 k^2}{2\sqrt{M_s M_{s'}}}$$

$$Y_{ss'}(\vec{k}) = \gamma_{ss'} \frac{\hbar^2 k^2}{2\sqrt{M_s M_{s'}}} \quad s, s' \in (1, 2). \tag{1.2}$$

It is seen from (1.2) that coefficients $x_{ss}(\vec{k}) = \frac{\hbar^2 k^2}{2 M_s}$ represent kinetic energies of molecules of the component s. Mass of the molecule is denoted by M_s. It is assumed that the mixing of Bose-amplitudes is proportional to kinetic energies of molecules. This is expressed by the non-diagonal terms $x_{ss'}(k); s' \neq s$. The quantities Δ_s are the Pauling's activation energies. These energies are of the order of magnitude of $L-S$ interaction, i. e. about 10^{-22} J. From the analytical structure of the Hamiltonian, it is obvious that the coefficients $Y_{ss'}(\vec{k})$ are related to virtual fusion processes of two molecules into a pair and also to the processes of pair desintegration. It is plausible to assume that the effects of these processes are proportional to kinetic energies of molecules and it was the reason for defining the given form of $Y_{ss'}$. Numbers $\gamma_{ss'}$ are the probabilities of pairing and desintegration and they can be calculated by quantum mechanical methods. We shall not make such a calculation. In further, we shall take $\gamma \lesssim 1$. Taking into account that the molecular masses M_s are of order of 10^{-22} g, we easily estimate order of magnitude of different terms appearing in the Hamiltonian (1.1), i. e. $\Delta_s \sim 10\, k_B$, $x_{ss'}, \sim 1\, k_B$, $Y_{ss'} \sim 1\, k_B$, where k_B is Boltzmann's constant.

The time evolution of the operators appearing in (1.1) can be found by the following transformation to the new Bose-operators b^+ and b:

$$B_s(\vec{k}) = \sum_\sigma [u_{s\sigma}(\vec{k})\, b_\sigma(\vec{k}) + v_{s\sigma}(\vec{k})\, b_\sigma^+(-\vec{k})] \quad s, \sigma \in (1,2). \tag{1.3}$$

The energies E, as well as the functions u and v are defined by the following system of equations

$$E u_{s\sigma}(\vec{k}) = \sum_{s'} [X_{ss'}(\vec{k})\, u_{s'\sigma}(\vec{k}) + Y_{ss'}(\vec{k})\, v_{s'\sigma}(\vec{k})]$$

$$-E v_{s\sigma}(\vec{k}) = \sum_{s'} [X_{ss'}(\vec{k})\, v_{s'\sigma}(\vec{k}) + Y_{ss'}(\vec{k})\, u_{s'\sigma}(\vec{k})]$$

$$\sum_{\sigma} [u_{s\sigma}(\vec{k})\, u_{s'\sigma}(\vec{k}) - v_{s\sigma}(\vec{k})\, v_{s'\sigma}(\vec{k})] = \delta_{ss'} \quad s, s', \sigma \in (1, 2) \tag{1.4}$$

The explicit form of energies and of the function u and v will not be quoted here. These formulae are very clumsy and they are not necessary for further analysis. The functions $u(\vec{k})$ and $v(\vec{k})$ are the even functions of $\vec{k}$ and this is the essential fact for our further considerations. This follows from the fact that the functions $X_{ss'}(\vec{k})$ and $Y_{ss'}(\vec{k})$ are the even functions of $\vec{k}$.

The transformation (1.3) leads to the diagonal form of the Hamiltonian (1.1):

$$H = \sum_{\sigma} E_{\sigma}(\vec{k})\, b_{\sigma}^{+}(\vec{k})\, b_{\sigma}(\vec{k}) \quad \sigma \in (1, 2). \tag{1.5}$$

Since the Hamiltonian (1.5) is diagonal, the time dependence of the operators b is the following

$$b_{\sigma}(\vec{k}, t) = b_{\sigma}(\vec{k}, 0)\, e^{-it\Omega_{\sigma}(\vec{k})} \quad \sigma \in (1,2);\ \hbar\,\Omega_{\sigma}(\vec{k}) = E_{\sigma}(\vec{k}) \tag{1.6}$$

Combining (1.6) and (1.4) we obtain:

$$B_s(\vec{k}, t) = \sum_{\nu} [\beta_{s\nu}^{(1)}(\vec{k}, t)\, B_{\nu}(\vec{k}, 0) + \beta_{s\nu}^{(2)}(\vec{k}, t)\, B^{\dagger}(-\vec{k}, 0)] \quad s, \nu \in (1,2)$$

$$\beta_{s\nu}^{(1)}(\vec{k}, t) = \sum_{\sigma} [u_{s\sigma}(\vec{k})\, u_{\nu\sigma}(\vec{k})\, e^{-i\Omega_{\sigma}(\vec{k})t} - v_{s\sigma}(\vec{k})\, v_{\nu\sigma}(\vec{k})\, e^{i\Omega_{\sigma}(\vec{k})t}] \tag{1.7}$$

$$\beta_{s\nu}^{(2)}(\vec{k}, t) = \sum_{\sigma} [u_{\nu\sigma}(\vec{k})\, v_{s\sigma}(\vec{k})\, e^{i\Omega_{\sigma}(\vec{k})t} - u_{s\sigma}(\vec{k})\, v_{\nu\sigma}(\vec{k})\, e^{-i\Omega_{\sigma}(\vec{k})t}] \quad s, \nu, \sigma \in (1,2).$$

The expressions for all necessary operator forms $B^{\dagger}B$, and BB can be easily found by the use of (1.7). These expressions are long and will not be quoted here.

The operators $B_s(\vec{k}, t)$, given be the formula (1.7), satisfy the condition (1.3) of energy conservation $H\{B(\vec{k}, 0), B^{\dagger}(\vec{k}, 0)\} = H\{B(\vec{k}, t), B^{\dagger}(\vec{k}, t)\}$. It is also seen from (1.7) that the time dependence of operators B is very specific, compared to the usual dependence of the type (1.6). This specific time dependence of the operators B causes some interesting effects, which will be analysed in the next section.

3. *Kinetic energies of particle pairs*

In order to analyse the kinetic energy of the system we start from the position vector of the center of mass of the system[6]. We can introduce the *stationary* vector

$$\vec{R}(t) = \sum_{s\vec{k}\vec{q}} \mu_s(\vec{k}-\vec{q})\, B_s^+(\vec{k}, t)\, B_s(\vec{q}, t) \quad s \in (1,2) \tag{2.1}$$

where:

$$B_s(\vec{k}, t) = e^{\frac{\hat{H}t}{i\hbar}}\, B_s(\vec{k}, o)\, e^{-\frac{\hat{H}t}{i\hbar}}$$

$$\mu_s(k-q) = \frac{1}{\mathcal{N}_s} \sum_{\vec{n}} \vec{n}\, e^{-i\vec{n}(\vec{k}-\vec{q})}; \quad \mu_s(o) = 0 \quad s \in (1,2). \tag{2.2}$$

In the last formula $\mathcal{N}_s$ is the number of molecules of the kind s.

The coresponding *nonstationary* one is given by:

$$\vec{R}(t) = \sum_{s\vec{k}\vec{q}} \mu_s(\vec{k}-\vec{q})\, A_s^+(\vec{k}, t)\, A_s(k, \vec{t}) \quad s \in (1,2) \tag{2.3}$$

where:

$$A_s(\vec{k}, t) = e^{\frac{\hat{H}t}{i\hbar}}\, B_s(\vec{k}, t)\, e^{-\frac{\hat{H}t}{i\hbar}}. \tag{2.4}$$

The operator $B_s(\vec{k}, t)$ is given by the formula (1.7). In further analysis only the expression (2.3) will be used. The velocity components of mass-center are given by:

$$p(t, \lambda) = \frac{d}{dt} R(t; \lambda) = \frac{1}{i\hbar} [R(t; \lambda), \hat{H}]; \quad \lambda \in (x, y, z). \tag{2.5}$$

In order to find the kinetic energy of the system, the Green's functions:

$$D_{\lambda\lambda'}(t) = \langle\langle \pi(t, \lambda) \mid \pi(0, \lambda') \rangle\rangle \tag{2.6}$$

will be analysed. It should be noticed that π is obtained from p by the transformation:

$$\mu_s(\vec{k}-\vec{q}) \to \mu_s(\vec{k}-\vec{q}) \sqrt{\frac{M_s}{2}}. \tag{2.7}$$

Nonstationary kinetic energy of the system is given as:

$$T(t) = T_{\mu}\{C_{\lambda\lambda'}(t)\} = \sum_{\lambda} C_{\lambda\lambda'}(t); \quad \lambda, \lambda' \in (x, y, z) \tag{2.8}$$

where $C_{\lambda\lambda'}(t)$ are the nonstationary correlation functions, corresponding to (2.6).

The functions $C_{\lambda\lambda'}(t)$ are of the form:

$$\sum_{ss'\sigma\sigma'} \langle A_{\sigma}^{+}(\vec{k}, 0)\, A_{\sigma'}^{+}(-\vec{k}, 0)\, A_{s'}(-\vec{k}, t)\, A_{s}(\vec{k}, t)\rangle \equiv \Gamma(\vec{k}, t) \tag{2.9}$$

and

$$\sum_{ss'\sigma\sigma'} \langle A_{\sigma}^{+}(\vec{k}, 0)\, A_{\sigma'}(\vec{k}, 0)\, A_{s}^{+}(\vec{k}, t)\, A_{s'}(\vec{k}, t)\rangle \equiv \Phi(\vec{k}, t). \tag{2.10}$$

The expressions of the type (2.9) and (2.10) are very complicated and will not be quoted here. The detailed analysis of such correlation functions one can find in Ref. 1. Here will be noticed that the imaginary part of Γ increases linearly with time, i. e.

$$Im\, \Gamma(\vec{k}, t) \sim -\frac{\Theta t}{4\hbar}; \quad \Theta = k_B T, \tag{2.11}$$

where T is absolute temperature. The other parts of Γ and Φ are the periodical function of time. Consequently, after long time periods the part of Γ, given by (2.11), becomes dominant.

The explicit expression for the kinetic energy will not be given here due to its tediousness. It is essentially to note that in the expression for the kinetic energy of the whole system the term proportional to (2.11) disappear. This result is physically justified, since the kinetic energy in whole must be the real quantity.

The kinetic energies of particle pairs, proportional to (2.11) are the following:

$$T_{diss}(\vec{k}_1, \vec{k}_2; t) = -\frac{\Theta t}{4\hbar} F(\vec{k}_1, \vec{k}_2) \tag{2.12}$$

where:

$$F(\vec{k}_1, \vec{k}_2) = \{[1 + \bar{n}_1(\vec{k}_1) + \bar{n}_1(\vec{k}_2)][\Omega_1(\vec{k}_1) + \Omega_1(\vec{k}_2)]^2 M_1 [v_{11}^2(\vec{k}_1) -$$

$$- v_{11}^2(\vec{k}_2)] + [1 + \bar{n}_2(\vec{k}_1) + \bar{n}_2(\vec{k}_2)][\Omega_2(\vec{k}_1) + \Omega_2(\vec{k}_2)]^2 M_2 [v_{22}^2(\vec{k}_1) -$$

$$- v_{22}^2(\vec{k}_2)] + [1 + \bar{n}_1(\vec{k}_1) + \bar{n}_2(\vec{k}_2)][\Omega_1(\vec{k}_1) + \Omega_2(\vec{k}_2)]^2 [M_2 v_{21}(\vec{k}_1) -$$

$$- M_1 v_{12}(\vec{k}_2)] + [1 + \bar{n}_1(\vec{k}_2) + \bar{n}_2(\vec{k}_1)][\Omega_1(\vec{k}_2) + \Omega_2(\vec{k}_1)]^2 [M_1 v_{12}^2(\vec{k}_1) -$$

$$- M_2 v_{21} (\vec{k}_2)] - [\bar{n}_1(\vec{k}_1) - \bar{n}_2 (\vec{k}_2)] [\Omega_1 (\vec{k}_1) - \Omega_2 (\vec{k}_2)] \times [M_1 u_{12}^2 (\vec{k}_2) +$$

$$+ M_2 u_{21}^2 (\vec{k}_1) + 2 (M_1 M_2)^{1/2} u_{12} (\vec{k}_2) u_{21} (\vec{k}_1)] + [\bar{n}_1 (\vec{k}_2) - \bar{n}_2 (\vec{k}_1)] [\Omega_1 (\vec{k}_2) -$$

$$- \Omega_2 (\vec{k}_1)] \times [M_1 u_{12}^2 (\vec{k}_1) + M_2 u_{21}^2 (\vec{k}_2) + 2 (M_1 M_2)^{1/2} u_{12} (\vec{k}_1) u_{21} (\vec{k}_2)]\} \times$$

$$\times \sum_{\lambda} | \mu (\vec{k}_1 - \vec{k}_2 ; \lambda)|^2 ; \quad n_s (\vec{k}) = \left[e^{\frac{E_s (\vec{k})}{\Theta}} - 1 \right]^{-1} ; \quad s \in (1,2). \tag{2.13}$$

The life-times of pairs can be expressed troughout T_{diss} in the following way:

$$\tau (\vec{k}_1, \vec{k}_2, t; \Theta) = \frac{- \hbar}{\mathrm{Im}\, T_{diss} (\vec{k}_1, \vec{k}_2, t)} = \frac{4\hbar}{\Theta F (\vec{k}_1 \vec{k}_2)} \frac{1}{t}. \tag{2.14}$$

It is clear from (2.13) and (2.14) that only the pairs with $\vec{k}_1 = \vec{k}_2$ and $\vec{k}_1 = -\vec{k}_2$ have the infinite life-times (u and v are the even functions of $\vec{k}$!). All other pairs disappear after a finite time. That means that due to the dissipativity processes the selection of pairs begins in the system and after a time there remain only pairs with parallel and antiparallel momenta. This process of disappearing of pairs whose momenta are not parallel or antiparallel is the ordering process caused by dissipation.

The conclusion obtained is of interest for biophysics since the actual biophysical theories are based on ideas that the dissipativity causes ordering of the system.

4. *Conclusion*

The analysis performed above can be summarized as follows:

1) Particle nonconservation leads to a sequence of dissipative processes. The imaginary parts of correlation functions, responsible for dissipativity, are linearly proportional to time.

2) Dissipativity of nonstationary processes does not change the total kinetic energy of the system but makes the selection of pairs of particles. After a sufficiently long time only the pairs with parallel as well as the antiparallel momenta remain in the system. In this manner dissipativity causes the ordering of the system what is in some manner compatible with Prigogine's ideas[7].

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NESTACIONARNI PROCESI I UREĐIVANJE

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UDK 538.95

Originalan naučni rad

Analizirani su nestacionarni procesi u dvo-komponentnoj gasnoj smeši. Pronađeno je vreme života parova koji se formiraju u nestacionarnim procesima. Pokazano je da samo parovi sa paralelnim i antiparalenim impulsima imaju beskonačno dugo vreme života. Svi ostali parovi posle izvesnog vremena nestaju. Ovaj efekat izazvan je disipativnošću koja karakteriše nestacionarne procese što znači da disipativnost zaziva uređivanje sistema.