Fluctuation phenomena in systems with diffusion-controlled reactions

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A new diagrammatic technique is used to investigate the annihilation reaction kinetics of particles executing diffusive motion in a medium. The effective reaction rate is found with allowance for the potential interaction between the particles, and the fluctuations in the steady-state regime with steady particle production are investigated. The deviations from a Poisson distribution in the steady-state regime are discussed.

In a number of situations the motion of excitations, quasiparticles, or defects in a crystal is well described by modeling it as a classical particle executing diffusive random walk. As examples, we can cite exciton-type excitations, radiation-induced defects in solids, electrons in ionic crystals, etc. Often, the diffusion process is accompanied by two-particle annihilation or recombination reactions in which defects and/or excitations participate (see Refs. 1–3). Similar phenomena occur in excitation quenching in solutions,[4] as well as in binary chemical reactions in weak solutions.[5]

The kinetics of diffusion-controlled reactions has been the subject of a substantial number of papers (in particular, Refs. 6–14; a comprehensive bibiliography can be found in Refs. 9, 10, and 14). The purpose of the majority of these is to compute the effective quenching, annihilation, or recombination rate for different specific systems. The calculations are, as a rule, based on various generalizations of the Smoluchowski method, which was developed back in 1917 for the description of the coagulation process (see Ref. 15). Computational schemes have also been developed in which the system of equations for the many-particle distribution functions are uncoupled with the aid of the Kirkwood approximation.[6,7,13] Much less thoroughly investigated is the problem of the fluctuation characteristics of the highly nonequilibrium steady state that arises when the annihilation proceeds concurrently with particle (excitation or defect) production. At the same time these fluctuation effects can be quite interesting. Thus, for example, numerical experiments[16,17] indicate the tendency of particles of two kinds to form clusters.

The present paper is devoted to a systematic analysis of the fluctuations in highly nonequilibrium media, in which the diffusion-controlled annihilation process occurs simultaneously with the steady production of the reacting particles. The analysis is carried out using the new version of the diagrammatic technique developed earlier by the present authors in Refs. 18–21 for classical reacting systems with diffusion.

1. FORMULATION OF THE PROBLEM

Let us consider a system of classical particles of two kinds, A and B, executing random walk with diffusion coefficients D_A and D_B in a continuous three-dimensional medium, and undergoing spontaneous decay and an irreversible annihilation (or recombination) reaction $A+B\to C$, the products of which do not have any further effect on the system. Let us assume that the particles A and B interact with each other via the pair potentials $u_{AA}(r)$, $u_{BB}(r)$, and $u_{AB}(r)$. Finally, we shall assume that uniform independent production of the reacting particles occurs in the medium. The probability for two particles A nd B located at a distance r from each other to react in unit time is given by the function $W(r)$, and the decay and uniform single-particle production are characterized by the intensities γ_A and γ_B, S_A and S_B.[1)]

The complete probability description of the system is furnished by the set $\{P_{N,M}\}$, whose elements $P_{N,M}(\mathbf{x}_1, \ldots, \mathbf{x}_N; \mathbf{y}_1, \ldots, \mathbf{y}_M; t)$ are the probability densities for finding in the system at time t N particles of the type A, located at the points $\mathbf{x}_1, \ldots, \mathbf{x}_N$, and M particles of the type B, located at the points $\mathbf{y}_1, \ldots, \mathbf{y}_M$. On account of the indistinguishablity of the particles, the functions $P_{N,M}$ are symmetric in the interchange $\mathbf{x}_i \leftrightarrow \mathbf{x}_j$ and $\mathbf{y}_i \leftrightarrow \mathbf{y}_j$. The normalization condition

$$\sum_{N,M=0}^{\infty} \int \frac{d\mathbf{x}_1 \ldots d\mathbf{x}_N\, d\mathbf{y}_1 \ldots d\mathbf{y}_M}{N!M!} \times P_{N,M}(\mathbf{x}_1, \ldots, \mathbf{x}_N; \mathbf{y}_1, \ldots, \mathbf{y}_M; t) = 1 \tag{1}$$

takes account of the nonconservation of the total number of particles of the two kinds.

The evolution of the system is governed by the principal kinetic equation

$$\begin{aligned}
\frac{\partial P_{N,M}}{\partial t} &= D_1 \sum_{i=1}^{N} \frac{\partial^2}{\partial \mathbf{x}_i^2} P_{N,M} + D_2 \sum_{i=1}^{M} \frac{\partial^2}{\partial \mathbf{y}_i^2} P_{N,M} \\
&\quad - \sum_{i,j} W(|\mathbf{x}_i - \mathbf{y}_i|) P_{N,M} \\
&\quad + \int W(|\mathbf{x}-\mathbf{y}|) P_{N+1,M+1}(\mathbf{x}_1, \ldots, \mathbf{x}_N, \mathbf{x}; \mathbf{y}_1, \ldots, \mathbf{y}_M, \mathbf{y}; t)\, d\mathbf{x}\, d\mathbf{y} \\
&\quad + D_1 \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{x}_i} \left\{ \frac{\partial}{\partial \mathbf{x}_i} \left[\sum_{i' \neq i} U_{11}(|\mathbf{x}_i - \mathbf{x}_{i'}|) \right.\right. \\
&\quad \left.\left. + \sum_{j=1}^{M} U_{12}(|\mathbf{x}_i - \mathbf{y}_j|) \right] P_{N,M} \right\} \\
&\quad + D_2 \sum_{j=1}^{M} \frac{\partial}{\partial \mathbf{y}_j} \left\{ \frac{\partial}{\partial \mathbf{y}_j} \left[\sum_{j' \neq j} U_{22}(|\mathbf{y}_j - \mathbf{y}_{j'}|) \right.\right. \\
&\quad \left.\left. + \sum_{i=1}^{N} U_{12}(|\mathbf{y}_j - \mathbf{x}_i|) \right] P_{N,M} \right\}
\end{aligned}$$

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$$+\gamma_1\int d\mathbf{x}_{N+1}P_{N+1,M}-N\gamma_1P_{N,M}$$

$$+\gamma_2\int d\mathbf{y}_{M+1}P_{N,M+1}-M\gamma_2P_{N,M}+S_1V^{-1}\sum_{i=1}^{N}P_{N-1,M}$$

$$-S_1P_{N,M}+S_2V^{-1}\sum_{j=1}^{M}P_{N,M-1}-S_2P_{N,M}, \qquad (2)$$

where V is the volume of the medium and we have $U_{ij}(r)=u_{ij}(r)/\Theta$, Θ being the temperature of the medium.

Doi[22] and, independently, Zel'dovich and Ovchinnikov[23] have proposed a formal "second quantization" procedure with the aid of which the system of equations (2) can be represented (see the Appendix) in the form

$$\frac{\partial}{\partial t}|\Phi\rangle=\hat{H}|\Phi\rangle, \qquad (3)$$

where $|\Phi\rangle$ is a state vector and $\hat{H}$ is a linear operator expressed in terms of the Bose creation and annihilation operators:

$$\hat{H}=-\sum_{\mathbf{k}}D_1k^2\hat{a}_{\mathbf{k}}^+\hat{a}_{\mathbf{k}}-\sum_{\mathbf{k}}D_2k^2\hat{b}_{\mathbf{k}}^+\hat{b}_{\mathbf{k}}+V^{-1}\sum_{\mathbf{k}}W(k)\hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}$$

$$-D_1V^{-1}\sum_{\mathbf{q},\mathbf{k}_1,\dots,\mathbf{k}_4}(\mathbf{q},\mathbf{q}+\mathbf{k}_2)U_{11}(q)\hat{a}_{\mathbf{k}_4}^+\hat{a}_{\mathbf{k}_3}^+\hat{a}_{\mathbf{k}_2}\hat{a}_{\mathbf{k}_1}\Delta(\mathbf{k}_4-\mathbf{k}_2-\mathbf{q})$$

$$\times\Delta(\mathbf{k}_1-\mathbf{k}_3-\mathbf{q})-D_2V^{-1}\sum_{\mathbf{q},\mathbf{k}_1,\dots,\mathbf{k}_4}(\mathbf{q},\mathbf{q}+\mathbf{k}_2)U_{22}(q)\hat{b}_{\mathbf{k}_4}^+\hat{b}_{\mathbf{k}_3}^+\hat{b}_{\mathbf{k}_2}\hat{b}_{\mathbf{k}}$$

$$\times\Delta(\mathbf{k}_4-\mathbf{k}_2-\mathbf{q})\Delta(\mathbf{k}_1-\mathbf{k}_3-\mathbf{q})-V^{-1}\sum_{\mathbf{q}\mathbf{k}_1\mathbf{p}_1\mathbf{p}}\{W(q)+(\mathbf{q},D_1(\mathbf{q}+\mathbf{k})$$

$$+D_2(\mathbf{q}-\mathbf{p}))U_{12}(q)\}\hat{a}_{\mathbf{k}_1}^+\hat{b}_{\mathbf{p}_1}^+\hat{a}_{\mathbf{k}}\hat{b}_{\mathbf{p}}\Delta(\mathbf{k}_1-\mathbf{k}-\mathbf{q})\Delta(\mathbf{p}-\mathbf{p}_1-\mathbf{q}) \qquad (4)$$

$$+\gamma_1\Big(\hat{a}_0-\sum_{\mathbf{k}}\hat{a}_{\mathbf{k}}^+\hat{a}_{\mathbf{k}}\Big)+\gamma_2\Big(\hat{b}_0-\sum_{\mathbf{k}}\hat{b}_{\mathbf{k}}^+\hat{b}_{\mathbf{k}}\Big)$$

$$+VS_1(\hat{a}_0^+-1)+VS_2(\hat{b}_0^+-1).$$

Here $W(k)$ and $U_{ij}(k)$ are the Fourier transforms of the corresponding functions and $\Delta(\mathbf{k})$ is the Kronecker symbol ($\Delta(\mathbf{k})=\delta_{\mathbf{k},0}$).

Thus, the state of the system is specified by the state vector $|\Phi\rangle$, whose evolution is governed by Eq. (3), which is similar to the Schrödinger equation—with imaginary time and a non-Hermitian Hamiltonian. Note that the procedure for computing the averages differs from the quantum-mechanical procedure (see (A.3)—(A.6) in the Appendix).

The operator formulation of the basic relations allows us to develop a diagrammatic perturbation theory technique. A detailed description can be found in Refs. 20 and 21. As the "free Hamiltonian," let us choose in this case

$$\hat{H}_0=-\sum_{\mathbf{k}}D_1k^2\hat{a}_{\mathbf{k}}^+\hat{a}_{\mathbf{k}}-\gamma_1\sum_{\mathbf{k}\neq0}\hat{a}_{\mathbf{k}}^+\hat{a}_{\mathbf{k}}$$

$$-\sum_{\mathbf{k}}D_2k^2\hat{b}_{\mathbf{k}}^+\hat{b}_{\mathbf{k}}-\gamma_2\sum_{\mathbf{k}\neq0}\hat{b}_{\mathbf{k}}^+\hat{b}_{\mathbf{k}},$$

all the remaining terms in $\hat{H}$ being lumped in $\hat{H}_{\text{int}}$.

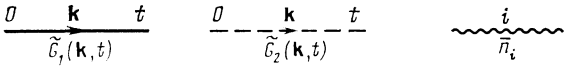
It follows from (A.7) and (A.8) that

$$\langle\hat{a}_0\hat{a}_0^+\rangle=\langle\hat{a}_0^+\hat{a}_0\rangle+1=\bar{N}_1+1, \qquad (5)$$
$$\langle\hat{a}_0\rangle=\bar{N}_1, \quad \langle\hat{a}_0^+\rangle=1.$$

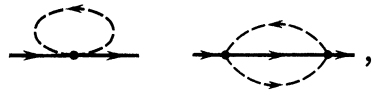
Therefore, the operators $\hat{a}_0$ and $\hat{a}_0^+$ can be considered to be c-numbers in the limit $\bar{N}_1\to\infty$, $V\to\infty$, $\bar{n}_1=\bar{N}_1/V=\text{const}$. Since we are interested only in the steady state, let us make the substitutions $\hat{a}_0\to\bar{n}_1V$, $b_0\to\bar{n}_2V$, $\hat{a}_0^+\to1$, $\hat{b}_0^+\to1$ in $\hat{H}_{\text{int}}$. These substitutions indicate that we are ignoring the fluctuations in the total number of particles in the system, and the whole procedure is similar to the procedure for separating out the condensate in the theory of the nonideal Bose gas.[24] The free Green's functions (GF) have the form

$$\tilde{G}_j(\mathbf{k},t)=\begin{cases}\exp(-(D_jk^2+\gamma_j)t] & \text{при } t>0\\ 0 & \text{при } t\leqslant0\end{cases}, \quad j=1,2.$$

It is convenient to introduce a diagrammatic notation. To do this, let us establish the correspondence between the GF and the condensate



and to each term in $\hat{H}_{\text{int}}$ assign a vertex where an ingoing line corresponds to an annihilation operator and an outgong line corresponds to a creation operator. The rules for calculating the diagrams are standard (see, for example, Ref. 24). Let us only note that, since the GF's vanish in the interval $t\leqslant0$ (i.e., there are only retarded GF's in this technique), diagrams of the type



etc., will be absent.

2. THE EFFECTIVE REACTION RATE

As we have already noted, quite a large number of papers (see, for example, Refs. 6–14) have been devoted to calculating the diffusion-controlled reaction rates in different systems, and this problem has been fairly well investigated. Below we show how the application of the diagrammatic technique allows us to arrive at results that generalize those found earlier for the various particular cases of the expression. At the same time this analysis serves as additional corroboration of the new diagrammatic technique.

The temporal evolution of the mean reacting-particle densities $\bar{n}_i=\bar{N}_i/V$ is, according to (3) and (A.8), governed by the equations

$$\dot{\bar{n}}_i=-V^{-2}\sum_{\mathbf{k}}W(k)\langle\hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\rangle-\gamma_i\bar{n}_i+V^{-1}S_i. \qquad (7)$$

We can, by expressing the density-density correlation function in terms of the operators

$$\langle\!\langle n_1(\mathbf{r}',t)n_2(\mathbf{r},t)\rangle\!\rangle=V^{-2}\sum_{\mathbf{k}}\langle\hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\rangle e^{i\mathbf{k}(\mathbf{r}'-\mathbf{r})}$$

rewrite the first term on the right-hand side of (7) in the more usual form

$$V^{-2}\sum_{\mathbf{k}}W(k)\langle\hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\rangle=\int d\mathbf{r}\,W(r)\langle\!\langle n_1(\mathbf{r},t)n_2(0,t)\rangle\!\rangle. \qquad (8)$$

Let us assume that the particles A and B are produced

with the same intensity S. In time the system will get into the state in which the particle creation and annihilation processes occur at the same rate (i.e., in which $\bar{n}_i = 0$). One of the most important characteristics of this steady state is the effective reaction rate

$$K_{eff} = \int d\mathbf{r}\, W(r) f(r), \tag{9}$$

where

$$f(r) = \langle\langle n_1(\mathbf{r}) n_2(0)\rangle\rangle / \bar{n}_1\bar{n}_2 = 1 + g(r).$$

It should be noted that the quantity K_{eff} can, in the general case, depend on $\bar{n}_i$. Knowing the reaction rate, we can find the steady-state value of $\bar{n}_i$:

$$K_{eff}\bar{n}_1\bar{n}_2 = SV^{-1} - \gamma_1\bar{n}_1, \quad \gamma_1\bar{n}_1 = \gamma_2\bar{n}_2.$$

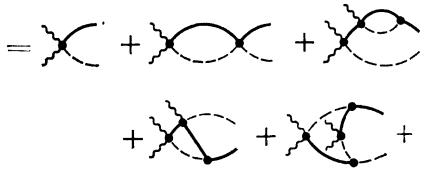
To find K_{eff}, let us use the diagrammatic technqiue developed above. We shall neglect the disintegration processes in the calculations, assuming them to be sufficiently weak (the limits of applicability of this assumption are indicated below).

We have, by definition,

$$g(r) = V^{-1}\sum_{\mathbf{k}}{}' g_k e^{i\mathbf{kr}}, \quad g_k = \langle \hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\rangle / V\bar{n}_1\bar{n}_2 .$$

The prime on the summation sign indicates that the summation is performed over all $\mathbf{k}$ except $\mathbf{k} = 0$. According to the rules for constructing the diagrams,

$\langle \hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\rangle = \langle \tilde{\hat{a}}_{\mathbf{k}}(t)\tilde{\hat{b}}_{-\mathbf{k}}(t)\,\hat{S}(t, -\infty)\rangle_0$



(10)

Therefore, we can write

$$\langle \hat{a}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\rangle = -V\bar{n}_1 n_2 \int_{-\infty}^{t} \bar{G}_1(\mathbf{k}, t-\tau)\bar{G}_2(-\mathbf{k}, t-\tau) I_k(\tau)\, d\tau,$$

introducing the quantity I_k.

In the steady state we have

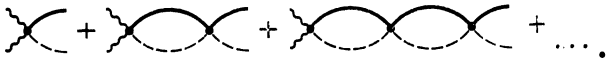
$$g_k = -I_k \int_0^{\infty} \bar{G}_1(\mathbf{k}, \tau)\bar{G}_2(-\mathbf{k}, \tau)\, d\tau,$$

or

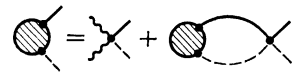
$$g_k = -I_k/Dk^2, \tag{11}$$

where $D = D_1 + D_2$.

Let us assume that the pump intensity S is so low that, in the steady state, the mean distance between the particles is much greater than the reaction radius, i.e., $\bar{n}_i r_0^3 \ll 1$. This allows us to separate out from the series (10) the diagrams containing the minimum number of condensate lines (specifically, two):

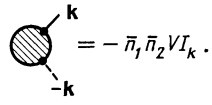


The summation of such ladder diagrams offers no difficulty, and amounts to the solution of the integral equation



(12)

where



$= -\bar{n}_1\bar{n}_2 V I_k$.

Analytically, Eq. (12) can be written in the form

$$I_k = W(k) + Dk^2 U_{12}(k) - V^{-1}\sum_{\mathbf{q}}{}' \{W(\mathbf{k}-\mathbf{q}) + D(\mathbf{k}-\mathbf{q}, \mathbf{k})\, U_{12}(\mathbf{k}-\mathbf{q})\}\, \frac{I_q}{Dq^2}. \tag{13}$$

It follows from the relations (8) and (13) that

$$K_{eff} = I_0.$$

Thus, to find K_{eff} to lowest order in the concentration, we must solve the integral equation (13) with the substitution

$$\sum_{\mathbf{k}}{}' \to (2\pi)^{-3} V \int d^3\mathbf{k}.$$

After carrying out an inverse Fourier transformation, we obtain from Eq. (13) the following equation for the correlation function $f(r)$:

$$D\,\mathrm{div}\,(\mathrm{grad}\, f + f\,\mathrm{grad}\, U_{12}) - Wf = 0. \tag{14}$$

A similar equation was obtained earlier in Refs. 6–10 through truncation of the chain of equations for the many-particle distribution functions with the aid of the Kirkwood approximation. It has also been derived in the theory of excitation quenching in solutions in the $U_{12} = 0$ case.[11,12]

For arbitrary $W(r)$ and $U_{12}(r)$ functions it is not possible to calculate in analytic form the correlation function f and the reaction rate K_{eff} from Eq. (14). As additional assumptions, we shall suppose that, first, the annihilation reaction can occur only when the two particles are at some distance r_0 or less from each other, i.e., that $W(r) = W_0$ for $r \leqslant r_0$ and $W(r) = 0$ when $r > r_0$; secondly, the variation of the potential U_{12} in the region $r < r_0$ can be ignored, i.e., $U_{12}(r) = U_0 = \text{const}$. Then, solving (14) in the regions $r < r_0$ and $r > r_0$ separately with the requirement that $|f(0)| < \infty$ and $f(\infty) = 1$, and matching the solutions at $r = r_0$, we find the function $f(r)$ and then the quantity K_{eff} from the formula (9):

$$K_{eff} = 4\pi D r_0 (1 - \mathrm{th}\,\lambda/\lambda)/(Jr_0(1 - \mathrm{th}\,\lambda/\lambda) + e^{U_0}\,\mathrm{th}\,\lambda/\lambda), \tag{15}$$

where

$$\lambda^2 = \frac{W_0 r_0^2}{D}, \quad J = \int_{r_0}^{\infty} \frac{dx}{x^2} e^{U_{12}(x)}.$$

The expression (15) includes a number of well-known results as limiting cases. In particular, in the absence of po-

tential interaction between the particles involved in the annihilation reaction (i.e., for $U_{12}(r)=0$), it gives[2)]

$$K_{eff}=4\pi Dr_0(1-\operatorname{th}\lambda/\lambda). \tag{16}$$

Notice that $\tau_0=r_0^2/D$ is the characteristic time spent by a particle in its diffusive walk inside a sphere of radius r_0. It can be called the diffusional collision time. Since W_0 gives the probability for annihilation in unit time when the particle separation is smaller than r_0 and the quantity λ^2 can be represented in the form $\lambda^2=W_0\tau_0$, we see that, for $\lambda^2\gg 1$, virtually every collision ends in annihilation, whereas for $\lambda^2\ll 1$ the relative fraction of such collisions is small. If $\lambda^2\gg 1$, then (16) gives $K_{\text{eff}}=4\pi Dr_0$, which coincides with Smoluchowski's result,[15] but if $\lambda^2\ll 1$, then $K_{\text{eff}}=(4\pi/3)W_0r_0^3$.

For $\lambda\gg 1$ and $U_{12}(r)\neq 0$, the formula (15) gives approximately $K_{\text{eff}}=4\pi D/J$. This is a classical result, first obtained by Debye.[5]

In conclusion, we give without derivation the expression for the effective reaction rate for the model of "hard spheres" with potential $U_{12}(r)=+\infty$ for $r\leqslant a$ and $U_{12}(r)=0$ for $r>a$ in the case when $a<r_0$:

$$K_{eff}=4\pi Dr_0\left(1-\frac{\operatorname{th}\lambda}{\lambda}\right)\left(1-\frac{\alpha\operatorname{ch}\alpha-\operatorname{sh}\alpha}{\lambda\operatorname{ch}\lambda-\operatorname{sh}\lambda}\right), \tag{17}$$

where $\alpha^2=W_0a^2/D$.

Allowance for the disintegration processes does not have much effect on the effective annihilation rates (15) and (17) when the conditions γ/W_0, $\gamma r_0^2/D\ll 1$ are fulfilled.

3. DENSITY FLUCTUATIONS IN THE STEADY STATE

Note that the GF's allow us to determine both the behavior of the local-density fluctuations in the steady state and the law according to which the overall (global) particle density approaches in time its steady-state value. It has been found by Zel'dovich and Ovchinnikov[23,25] that, in three-dimensional systems in which an irreversible bimolecular reaction of the type $A+A\leftrightarrow B$ or $A\leftrightarrow B+C$ occurs, and the stationary state is a thermodynamic equilibrium one, the equilibrium is established not exponentially rapidly, as the law of mass action predicts, but in a power-law fashion: $\delta n\sim(D_{\text{eff}}t)^{-3/2}$, where D_{eff} has the meaning of an effective diffusion coefficient. Using the GF apparatus, we show that similar power-law dependences obtain also in two-component systems in which thermodynamic equilibrium does not occur, and whose steady state is determined by the competition between an external uniform independent pumping of the particles and the irreversible reaction between them.

In a system consisting of particles A and B, there are four single-particle GF's, which can conveniently be written in the form of a 2×2 matrix:

$$\hat G(\mathbf{k};\,t_1,\,t)=\left\langle \hat T\left\{\begin{pmatrix}\hat a_{\mathbf{k}}(t_1)\hat a_{\mathbf{k}}^{+}(t) & \hat b_{\mathbf{k}}(t_1)\hat a_{\mathbf{k}}^{+}(t)\\ \hat a_{\mathbf{k}}(t_1)\hat b_{\mathbf{k}}^{+}(t) & \hat b_{\mathbf{k}}(t_1)\hat b_{\mathbf{k}}^{+}(t)\end{pmatrix}\hat S(t_1=-\infty)\right\}\right\rangle_0 .$$

The absence of off-diagonal—in k—single-particle averages is due to the conservation of the wave vector of each vertex of the diagramatic technique as a separate entity.

The matrix $\hat G$ satisfies the Dyson equation

$$\hat G(\mathbf{k};\,t,\,0)=\hat{\tilde G}(\mathbf{k},\,t)-\int\hat{\tilde G}(\mathbf{k},\,\tau_1)\hat\Sigma(\mathbf{k};\,\tau_2,\,\tau_1)\hat G(\mathbf{k};\,t,\,\tau_2)\,d\tau_1\,d\tau_2, \tag{18}$$

where $\tilde G$ and $\hat\Sigma$ are the free-diffusion GF and "mass operator" (MO) matrices, the matrix $\tilde G$ being, by definition, diagonal. In the steady states the time variables enter into the GF and MO only in the form of a difference, e.g.,

$$\hat\Sigma(\mathbf{k};\,\tau_2,\,\tau_1)=\hat\Sigma(\mathbf{k},\,\tau_2-\tau_1).$$

This enables us to solve Eq. (18) without difficulty; after a Fourier transformation in the time it assumes the form

$$\hat G(\mathbf{k},\,\omega)=\hat{\tilde G}(\mathbf{k},\,\omega)-\hat{\tilde G}(\mathbf{k},\,\omega)\hat\Sigma(\mathbf{k},\,\omega)\hat G(\mathbf{k},\,\omega).$$

The solution to this equation is easy to obtain:

$$\hat G(\mathbf{k},\,\omega)=\Omega^{-1}(\mathbf{k},\,\omega)\begin{pmatrix}\tilde G_{22}^{-1}(\mathbf{k},\,\omega)+\Sigma_{22}(\mathbf{k},\,\omega) & -\Sigma_{12}(\mathbf{k},\,\omega)\\ -\Sigma_{21}(\mathbf{k},\,\omega) & \tilde G_{11}^{-1}(\mathbf{k},\,\omega)+\Sigma_{11}(\mathbf{k},\,\omega)\end{pmatrix}, \tag{19}$$

where

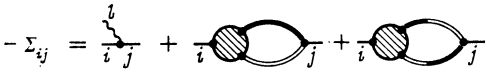
$$\Omega(\mathbf{k},\,\omega)=(\tilde G_{11}^{-1}(\mathbf{k},\,\omega)+\Sigma_{11}(\mathbf{k},\,\omega))\,(\tilde G_{22}^{-1}(\mathbf{k},\,\omega)+\Sigma_{22}(\mathbf{k},\,\omega))-\Sigma_{12}(\mathbf{k},\,\omega)\Sigma_{21}(\mathbf{k},\,\omega). \tag{20}$$

It is clear that all the information about the asymptotic forms of the GF's is contained in the roots of the equation $\Omega(\mathbf{k},\omega)=0$.

In the absence of disintegration processes, the free-diffusion GF, $\tilde G_{jj}$, posseses a pole $\omega=-iD_jk^2$. Let us show that the total GF also possesses a diffusion-type singularity, i.e., that the equation $\Omega(\mathbf{k},\omega)=0$ has a root that, as $\mathbf{k}\to 0$, behaves like $\omega=-iD_{\text{eff}}k^2$, where D_{eff} is a constant having the dimensions of a diffusion coefficient. To do this, let us prove that

$$\lim_{\mathbf{k},\omega\to 0}[\Sigma_{11}(\mathbf{k},\,\omega)\Sigma_{22}(\mathbf{k},\,\omega)-\Sigma_{12}(\mathbf{k},\,\omega)\Sigma_{21}(\mathbf{k},\,\omega)]=0. \tag{21}$$

Indeed, the expression for the MO has the form

$-\Sigma_{ij}=$  (22)

The thick lines here represent the total GF's and

represents total irreducible triple vertex. The indices in the diagrams indicate the types of ingoing and outgoing lines. By comparing the expression (22) for $j=1$ and $j=2$, we can easily verify that

$$\lim_{\mathbf{k},\omega\to 0}\Sigma_{i1}(\mathbf{k},\,\omega)=\lim_{\mathbf{k},\omega\to 0}\Sigma_{i2}(\mathbf{k},\,\omega),\qquad i=1,2.$$

From this we immediately obtain (21).

It should be noted that, in the analogous one-component system ($A+A\to 0$ in the presence of uniform generation), allowance for the reactions between the particles causes the diffusion-type singularities in the GF to disappear. In Refs. 20 and 21 we show that in this case

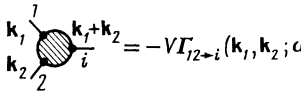
$$G^{-1}(\mathbf{k},\ \omega)=Dk^2+2\bar{n}K_{eff}-i\omega. \tag{23}$$

Since we are interested in the case of low concentrations $\bar{n}_i$, let us separate out from the whole set of diagrams for Σ_{ij} the ladder diagrams as being of the lowest power in $\bar{n}_i$ among all others, and then sum them in all orders of perturbation theory. Then we have

$$i,\ j=1,\ 2; \quad l\neq i. \tag{24}$$

The effective triple vertex entering into (24) can be found from the equation

Let us, setting



write (25) in analytic form:

$$\Gamma_{12\to i}(\mathbf{k}_1,\mathbf{k}_2;\ \omega)=W(k_j)+D_i(\mathbf{k}_j,\mathbf{k}_1+\mathbf{k}_2)U_{12}(k_j)$$
$$-V^{-1}\sum_{\mathbf{q}}{}'\{W(q)$$
$$+(\mathbf{q},D_1(\mathbf{q}+\mathbf{k}_1)+D_2(\mathbf{q}-\mathbf{k}_2))U_{12}(q)\}$$
$$\times\{[G_{11}(\mathbf{k}_1+\mathbf{q})G_{22}(\mathbf{k}_2-\mathbf{q})]_\omega$$
$$\times\Gamma_{12\to i}(\mathbf{k}_1+\mathbf{q},\mathbf{k}_2-\mathbf{q};\ \omega)+[G_{12}(\mathbf{k}_1+\mathbf{q})G_{21}(\mathbf{k}_2-\mathbf{q})]_\omega$$
$$\times\Gamma_{12\to i}(\mathbf{k}_2-\mathbf{q},\mathbf{k}_1+\mathbf{q};\ \omega)\},\quad j\neq i. \tag{26}$$

Here and below the symbol $[GG]_\omega$ corresponds to the Fourier transform of the product of two GF. From the form of expression (26) we obtain the following relation between the effective vertices:

$$\Gamma_{12\to 1}(\mathbf{k},\ \pm\mathbf{k};\ \omega)=\Gamma_{12\to 2}(\mathbf{k},\ \pm\mathbf{k};\ \omega),$$

with (cf. (13))

$$\Gamma_{12\to i}(\mathbf{k},\ -\mathbf{k};\ 0)=I_k,\quad \Gamma_{12\to i}(0,\ 0;\ 0)=K_{eff}.$$

Comparing the diagrammatic equations (24) and (25), we easily see that

$$\hat{\Sigma}(k.\ \omega)=\begin{pmatrix}\bar{n}_2\Gamma_{12\to 1}(\mathbf{k},0;\ \omega) & \bar{n}_2\Gamma_{12\to 2}(\mathbf{k},0;\ \omega)\\ \bar{n}_1\Gamma_{12\to 1}(0,\mathbf{k};\ \omega) & \bar{n}_1\Gamma_{12\to 2}(0,\mathbf{k};\ \omega)\end{pmatrix}. \tag{27}$$

The expressions (19), (26), and (27), taken together, constitute a closed system of equations for the determination of the GF's.

The quantities Σ_{ij} are small, since they are proportional to the mean concentrations of the reacting particles, and their contribution to $\hat{G}(\mathbf{k},\omega)$ is significant only at small $\mathbf{k}$ and ω values, i.e., in the vicinity of the singular point of the GF. Therefore, we shall replace the Σ_{ij} entering into (19) by their values at $\mathbf{k}$, $\omega=0$:

$$\hat{\Sigma}(0,0)=K_{eff}\begin{pmatrix}\bar{n}_2 & \bar{n}_2\\ \bar{n}_1 & \bar{n}_1\end{pmatrix}$$

and solve the equation $\Omega(\mathbf{k},\omega)=0$ for ω:

$$\omega_1(\mathbf{k})\approx -iD_{eff}k^2, \tag{28}$$
$$\omega_2(\mathbf{k})\approx -i\left(\frac{D_1\bar{n}_2+D_2\bar{n}_1}{\bar{n}_1+\bar{n}_2}k^2+K_{eff}(\bar{n}_1+\bar{n}_2)\right),$$

where $D_{\text{eff}}=(D_1\bar{n}_1+D_2\bar{n}_2)/(\bar{n}_1+\bar{n}_2)$ is the effective diffusion coefficient.

Let us consider the behavior of the local particle density fluctuations in the steady state. Specifically, we shall be interested in the quantity

$$\langle\langle\delta n_j(\mathbf{r},\ t)\delta n_i(0,\ 0)\rangle\rangle=\langle\langle n_j(\mathbf{r},\ t)n_i(0,\ 0)\rangle\rangle-\bar{n}_i\bar{n}_j. \tag{29}$$

The angle brackets in the present case denote averaging over the steady state. Using $\langle\delta n_1\delta n_1\rangle$ as an example, we show how the correlators (29) are related with the GF. By means of the operator formulation and the relation (6), we obtain

$$\langle\!\langle\delta n_1(\mathbf{r},t)\delta n_1(0,0)\rangle\!\rangle$$
$$=\bar{n}_1V^{-1}\sum_{\mathbf{k}}{}'\langle\hat{T}\{\hat{\tilde{a}}_{\mathbf{k}}(t)\hat{\tilde{a}}_{\mathbf{k}}^{+}(0)\hat{S}(t,-\infty)\}\rangle_0 e^{i\mathbf{kr}}$$
$$+V^{-2}\sum_{\mathbf{k}}{}'\langle T\{\hat{\tilde{a}}_{\mathbf{k}}(t)\hat{\tilde{a}}_{-\mathbf{k}}(0)\hat{S}(t,-\infty)\}\rangle_0 e^{i\mathbf{kr}} \tag{30}$$
$$+V^{-2}\sum_{\mathbf{k},\mathbf{q}}{}'\langle\hat{T}\{\hat{\tilde{a}}_{\mathbf{k}}(t)\hat{\tilde{a}}_{\mathbf{k}+\mathbf{q}}^{+}(0)\hat{\tilde{a}}_{\mathbf{q}}(0)\hat{S}(t,-\infty)\}\rangle_0 e^{i\mathbf{kr}}.$$

Note that the terms of the diagrammatic expansions of the second and third terms on the right-hand side of (30) always contain at least two condensate lines. Therefore, in the case of small steady-state values of the reacting-particle densities these terms are of order $\bar{n}^2$, and are small compared to the first term, in which it is not difficult to distinguish the GF. Consequently,

$$\langle\langle\delta n_j(\mathbf{r},\ t)\delta n_i(0,\ 0)\rangle\rangle\approx\bar{n}_iG_{ij}(r,\ t). \tag{31}$$

Hence, taking account of (28), we obtain in the case when $(\bar{n}_1+\bar{n}_2)K_{\text{eff}}t\gg 1$ the approximate result

$$\langle\!\langle\delta n_j(0,t)\delta n_i(0,0)\rangle\!\rangle$$
$$\approx(\bar{n}_1+\bar{n}_2)^{-1}\begin{pmatrix}\bar{n}_1^2 & -\bar{n}_1\bar{n}_2\\ -\bar{n}_1\bar{n}_2 & \bar{n}_2^2\end{pmatrix}(D_{eff}t)^{-3/2}$$
$$+K_{eff}^{-1}(\bar{n}_1+\bar{n}_2)^{-2}\begin{pmatrix}\bar{n}_1^2(D_2-D_1) & 0\\ 0 & \bar{n}_2^2(D_1-D_2)\end{pmatrix}(D_{eff}t)^{-5/2}. \tag{32}$$

In a one-component system, the damping of the density fluctuations proceeds differently. From (23) it follows that

$$\langle\langle\delta n(0,\ t)\delta n(0,\ 0)\rangle\rangle\approx\bar{n}(Dt)^{-3/2}\exp(-2\bar{n}K_{eff}t),$$

i.e., a local-density fluctuation that arises at some point of the system dissipates according to an exponential law. This difference is explained by the fact that the special type of fluctuations that takes place in a system with two reactants:

the fluctuations in the local-density difference

$$\delta n_-(\mathbf{r}, t)=\delta n_1(\mathbf{r}, t)-\delta n_2(\mathbf{r}, t),$$

do not occur in a one-component system. The role played by these fluctuations in the behavior of a system supporting a reaction and diffusion has been repeatedly noted in the literature (see Refs. 10, 25, and 26). Since in the absence of disintegration processes (i.e., for $\gamma_1=\gamma_2=0$) $\bar{n}_1-\bar{n}_2=\text{const}$, there arises in the course of the evolution of the system a situation that, in a sense, is similar to the one described by the quantum-mechanical Goldstone theorem, which asserts that the energy spectrum of the local fluctuations of a quantity that is conserved as a whole in the system is gapless. Indeed, using (28) and (31), we find that, for small $\mathbf{k}$ and ω in the steady state,

$$\langle\langle \delta n_- \delta n_- \rangle\rangle_{\mathbf{k},\omega}=i(\bar{n}_1+\bar{n}_2)(\omega-\omega_1(\mathbf{k}))^{-1}.$$

Let us note that, to take account of extermely weak disintegration processes (i.e., those for which $\gamma_1 \ll \bar{n}_2 K_{\text{eff}}$, $\gamma_2 \ll \bar{n}_1 K_{\text{eff}}$, we need make only one change: the quantity $\omega_1(k)$ from the relations (28) will assume the form

$$\omega_1(\mathbf{k}) \approx -i(D_{eff}k^2+\gamma_{eff}),$$

where $\gamma_{\text{eff}}=(\bar{n}_1\gamma_1+\bar{n}_2\gamma_2)/(\bar{n}_1+\bar{n}_2)$. Therefore, each term in the estimate (32) will have an additional factor, specifically, the factor $\exp(-\gamma_{\text{eff}}t)$.

4. DEVIATIONS FROM THE POISSON DISTRIBUTION

In the absence of reactions, the particle number distribution inside a fixed volume element will be a Poisson distribution. For such a distribution we have the relation

$$\overline{\delta N^2}/\bar{N}=1. \tag{33}$$

Here $\bar{N}$ is the average number of particles in the region of the volume Ω and $\delta N=N-\bar{N}$.

A reaction and a potential interaction between the particles give rise to deviations from the law (33), i.e., to the suppression or enhancement of the particle-number fluctuations, as compared to the fluctuations dictated by the Poisson law. It is not difficult to verify that these deviations are determined by the pair correlation function for the particles of one species:

$$\overline{\delta N_i^2}/\bar{N}_i=1+\bar{n}_i\Omega^{-1}\int_{(\Omega)} d\mathbf{r}_1\, d\mathbf{r}_2\, g_{ii}(|\mathbf{r}_1-\mathbf{r}_2|). \tag{34}$$

The Fourier transform of the correlation function is given by the expression

$$g_{ii}(k)=-2\int G_{ii}(\mathbf{k},\tau)G_{ji}(-\mathbf{k},\tau)\,d\tau\, I_k, \quad j\neq i. \tag{35}$$

We shall choose as the volume element Ω a sphere of radius R that is large compared to the reaction radius r_0 ($R \gg r_0$). As follows from (34), to find the mean fluctuation intensity in such a large region, it is sufficient to know only $g_{ii}(k)$ for small values of $\mathbf{k}$. Therefore, we can approximately set $I_k \approx I_0 = K_{\text{eff}}$ in Eq. (35).

Let us first consider a system in which particles of the same kind annihilate each other (i.e., in which a reaction of the type $A+A\to 0$ occurs). In this case the GF has the form (23), and for $g(r)$ in the region $r \gg r_0$ we have

$$g(r)=-(16\pi r_c^2\bar{n})^{-1}e^{-r/r_c}/r, \tag{36}$$

where $r_c=(D/2\bar{n}K_{\text{eff}})^{1/2}$ is the correlation length. Substituting (36) into (34), and performing the integration, we find

$$\overline{\delta N^2}/\bar{N}=1-{}^1/_4 F(2R/r_c), \tag{37}$$

where the function $F(x)$ is defined as

$$F(x)=1-(1+x)e^{-x}. \tag{38}$$

In particular, for $r_0 \ll R \ll r_c$, we have

$$\overline{\delta N^2}/\bar{N} \approx 1-R^2/2r_c^2, \tag{39}$$

whereas for regions of large radius ($R \gg r_c$) we have

$$\overline{\delta N^2}/\bar{N} \approx {}^3/_4. \tag{40}$$

A comparison of the expressions found above with the formula (33) shows that the annihilation of particles of the same kind leads to the suppression of the large-scale fluctuations in comparison with the fluctuations described by the Poisson distribution. At the same time the particle number fluctuations inside a region with dimension smaller than the correlation length r_c are close to being Poisson fluctuations, i.e., at these scales the particles behave as independent particles.

Another situation obtains in the case of annihilation of unlike particles ($A+B\to 0$). Let us first give the results for the case when the two kinds of particles have the same average concentration (i.e., when $\bar{n}_A=\bar{n}_B=\bar{n}$) in the steady-state regime, and their diffusion coefficients are equal ($D_A=D_B=D$). We shall also take account of the weak single-particle disintegration processes ($A\to 0$, $B\to 0$), assuming that the disintegration rate γ is low (i.e., that $\gamma \ll \bar{n}K_{\text{eff}}$). Under these assumptions the pair correlation function is given by the expression

$$g(r)=(32\pi r_c^2\bar{n})^{-1}(e^{-r/r_\gamma}-e^{-r/r_c})/r, \tag{41}$$

where $r_\gamma=(D/\gamma)^{1/2}$ and $r_c=(D/2\bar{n}K_{\text{eff}})$, with $r_\gamma \gg r_c$. The mean fluctuation of the particle number in a region of radius R is

$$\overline{\delta N^2}/\bar{N}=1+{}^1/_8(r_\gamma/r_c)^2F(2R/r_\gamma)-{}^1/_8F(2R/r_c), \tag{42}$$

where the fluctuation $F(x)$ is defined above.

In the case of the annihilation reaction between unlike particles the spatial fluctuations are enhanced in comparison with the Poisson fluctuations. As follows from (42), this deviation is enhanced in the region $r_0 \ll R \ll r_c$, but is still fairly small:

$$\overline{\delta N^2}/\bar{N} \approx 1+{}^1/_3(R/r_c)^3. \tag{43}$$

The deviations increase sharply when we go over into the region[3] $r_c \ll R \ll r_\gamma$:

$$\overline{\delta N^2}/\bar{N} \approx {}^1/_4 (R/r_c)^2. \tag{44}$$

Finally, in the region $R \gg r_\gamma$ the deviations cease to grow, and settle at a constant fairly high level:

$$\overline{\delta N^2}/\bar{N} \approx {}^1/_8 (r_\gamma/r_c)^2. \tag{45}$$

The sharp increase in the spatial fluctuations in the particle number (the "clustering effect"), that occurs in the process of annihilation of unlike particles was observed earlier in numerical experiments.[16,17] The physical cause of this effect is fairly simple. In the case of independent random generation, more particles of one (for definiteness, the first) kind can be produced in some region of the medium than those of the other (second) kind. The particles of the second kind quickly find for themselves "partners," and undergo annihilation; as a result only particles of the first kind will be left over in the region. The clusters produced can dissipate through diffusion or as a result of a slow single-particle disintegration. There are characteristic differences between these two processes: the greater the spatial dimension of the cluster, the slower its diffusive spreading, whereas for the single-particle disintegrations the size of the cluster is not important. We emphasize that the effects of the formation of spatial clusters in annihilation reactions involving two kinds of particles were first discussed by Zel'dovich and Ovchinnikov.[27,28]

In conclusion, we give the expression for the pair correlation function in the more general case when the two kinds of particles have different diffusion coefficients D_A and D_B, as well as different average steady-state concentrations:

$$g_{ii}(r) = \frac{\bar{n}_i K_{eff}}{4\pi r} \left\{ \frac{\bar{n}_i}{(\bar{n}_1+\bar{n}_2)^2 D_{eff}} e^{-r/r_\gamma} + (-1)^i \times \frac{\bar{n}_1 D_1 - \bar{n}_2 D_2}{(\bar{n}_1+\bar{n}_2)(\bar{n}_1 D_1^2 + \bar{n}_2 D_2^2)} e^{-r/\tilde{r}_c} - \frac{\bar{n}_j D_j^2}{(\bar{n}_1+\bar{n}_2) D_{eff} (\bar{n}_1 D_1^2 + \bar{n}_2 D_2^2)} e^{-r/r_c} \right\},$$
$$i = 1, 2; \quad j \neq i, \tag{46}$$

where

$$r_\gamma = (D_{eff}/\gamma_{eff})^{1/2}, \quad r_c = (D_1 D_2/(\bar{n}_1+\bar{n}_2) D_{eff} K_{eff})^{1/2},$$
$$\tilde{r}_c = ((D_1+D_2)/(\bar{n}_1+\bar{n}_2) K_{eff})^{1/2}.$$

Here it is implied that the disintegration rate is low (i.e., that $\gamma_1 \ll \bar{n}_2 K_{\text{eff}}$ and $\gamma_2 \ll \bar{n}_1 K_{\text{eff}}$), and therefore $r_\gamma \gg r_c, \tilde{r}_c$. For the particle-number fluctuations in a volume with $R \gg r_\gamma$ we obtain

$$\overline{\delta N_i^2}/\bar{N}_i \approx i\bar{n}_i^3 K_{eff}/(\bar{n}_1+\bar{n}_2)^2 \gamma_{eff}. \tag{47}$$

In the case when r_c, $\tilde{r}_c \ll R \ll r_\gamma$ we have

$$\overline{\delta N_i^2}/\bar{N}_i \approx 2\bar{n}_i^3 K_{eff} R^2/(\bar{n}_1+\bar{n}_2)^2 D_{eff}. \tag{48}$$

It is easy to see that, if the diffusion coefficients D_1 and D_2 are of the same order of magnitude, then r_c and $\tilde{r}_c$ will also be quantities of the same order of magnitude. In the opposite case (e.g., in the $D_1 \gg D_2$ case), when the particles of one kind diffuse much faster than the particles of the other kind, the inequality $\tilde{r}_c \gg r_c$ is satisfied. In this case, at the scale $R \ll r_c$, the deviations of the fluctuations from the Poisson fluctuations are small.

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APPENDIX

With the set $\{P_{N,M}\}$ is associated the system's state vector

$$|\Phi(t)\rangle = \sum_{N,M=0}^{\infty} (N!\,M!)^{-1} V^{(N+M)/2} \int P_{N,M}(\{\mathbf{x}\}_N, \{\mathbf{y}\}_M; t) \times \prod_{i=1}^{N} \prod_{j=1}^{M} \hat{\psi}_1^+(\mathbf{x}_i) \hat{\psi}_2^+(\mathbf{y}_j)\, d\mathbf{x}_i\, d\mathbf{y}_j |0\rangle, \tag{A.1}$$

where

$$[\hat{\psi}_i(\mathbf{r}), \hat{\psi}_j^+(\mathbf{r}')] = \delta_{ij}\delta(\mathbf{r}-\mathbf{r}'), \quad \hat{\psi}_i|0\rangle = 0 = \langle 0|\hat{\psi}_i^+.$$

We can, using the identity

$$\langle 0| V^{-(N+M)/2} \prod_{i=1}^{N} \prod_{j=1}^{M} \hat{\psi}_1(\mathbf{x}_i) \hat{\psi}_2(\mathbf{y}_j) |\Phi(t)\rangle = P_{N,M}(\{\mathbf{x}\}_N \{\mathbf{y}\}_M; t),$$

write the system (2) in the form of the Schrödinger equation with imaginary time:

$$\frac{\partial}{\partial t} |\Phi(t)\rangle = \hat{H} |\Phi(t)\rangle, \tag{A.2}$$

where the operator $\hat{H}$ is expressed in terms of $\hat{\psi}_i(\mathbf{x})$ and $\hat{\psi}_i^+(\mathbf{x})$. We obtain the expression (4) after carrying out a standard expansion of the operators $\hat{\psi}_i$ and $\hat{\psi}_i^+$ in terms of plane waves:

$$\hat{\psi}_1^+(\mathbf{x}) = V^{-1/2} \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^+ e^{-i\mathbf{kx}}, \quad \hat{\psi}_1(\mathbf{x}) = V^{-1/2} \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}} e^{i\mathbf{kx}},$$

and similarly for $\hat{\psi}_2$, $\hat{\psi}_2^+$ and $\hat{b}_{\mathbf{k}}$, $\hat{b}_{\mathbf{k}}^+$.

The ensemble average

$$\bar{A} = \sum_{N,M=0}^{\infty} \int (N!M!)^{-1} \prod_{i=1}^{N} \prod_{j=1}^{M} d\mathbf{x}_i\, d\mathbf{y}_j\, A(\{\mathbf{x}\}_N, \{\mathbf{y}\}_M) \times P_{N,M}(\{\mathbf{x}\}_N, \{\mathbf{y}\}_M; t) \tag{A.3}$$

for an arbitrary quantity A can be written in the form

$$\bar{A} = \langle\Phi|\hat{A}|\Phi\rangle \equiv \langle\hat{A}\rangle \equiv \langle\langle A\rangle\rangle, \tag{A.4}$$

where the quantity A is associated, in accordance with rules similar to the quantum-mechanical rules, with the operator $\hat{A}$ and $|\Phi\rangle$ is a fixed normalization vector:

$$|\Phi\rangle = \exp\left\{V^{-1/2} \int (\hat{\psi}_1^+(\mathbf{x}) + \hat{\psi}_2^+(\mathbf{x}))\, d\mathbf{x}\right\} |0\rangle = \exp\{\hat{a}_0^+ + \hat{b}_0^+\} |0\rangle. \tag{A.5}$$

The normalization condition (1) can be represented as

$$\langle\Phi|\Phi\rangle = 1. \tag{A.6}$$

The normalization vector $|\Phi\rangle$ possesses the property that

$$\hat{\psi}_i(\mathbf{x})|\Phi\rangle = V^{-1/2}|\Phi\rangle, \text{ или } \hat{a}_{\mathbf{k}}|\Phi\rangle = \hat{b}_{\mathbf{k}}|\Phi\rangle = \Delta(\mathbf{k})|\Phi\rangle.$$

Therefore, the following identities always obtain

$$\langle\hat{\psi}_i^+(\mathbf{x})\rangle = V^{-1/2}, \text{ или } \langle\hat{a}_{\mathbf{k}}^+\rangle = \langle\hat{b}_{\mathbf{k}}^+\rangle = \Delta(\mathbf{k}), \quad \text{(A.7)}$$

$$\overline{N}_i/V = \langle\hat{\psi}_i^+\hat{\psi}_i\rangle = \langle\hat{\psi}_i\rangle V^{-1/2}, \text{ или } \langle\hat{a}_0\rangle = \overline{N}_1, \ \langle\hat{b}_0\rangle = \overline{N}_2, \quad \text{(A.8)}$$

where $\overline{N}_i$ is the mean total number of the i-particles in the system.

The double-time correlation function for the quantities A and B has the form (for definiteness $t' > t$):

$$\begin{aligned}\langle\langle A(t')B(t)\rangle\rangle &= \langle\Phi|\hat{A}\exp(\hat{H}(t'-t))\hat{B}|\Phi(t)\rangle \\ &= \langle\Phi|\hat{T}\{\tilde{A}(t')\tilde{B}(t)\hat{S}(t',-\infty)\}|\tilde{\Phi}(-\infty)\rangle \\ &\equiv \langle\hat{T}\{\tilde{A}(t')\tilde{B}(t)\hat{S}(t',-\infty)\}\rangle_0, \quad \text{(A.9)}\end{aligned}$$

where $\hat{S}(t',-\infty) = \hat{T}\exp\left\{\int_{-\infty}^{t'}\tilde{H}_{\text{int}}(\tau)d\tau\right\}$ and the tilde indicates the operators and state vector in the interaction representation.

[1)]Below, in order to simplify the rather unwieldy perturbation-theory expressions, we shall sometimes call the particles A and B particles of the kinds 1 and 2, respectively, and label the quantities characterizing them by the indices 1 and 2.

[2)]A similar expression is obtained in Ref. 12 in an analysis of the "mixed" mechanism of excitation quenching in solutions.

[3)]The intermediate asymptotic form (44) was recently obtained also by Burlatskiĭ and Ovchinnikov[29] on the basis of macroscopic kinetic equations for the fluctuating concentrations with allowance for the random spread in the production rates.

[1]V. M. Agranovich and M. D. Galanin, Perenos énergii élektronnogo vozbuzhdeniya v kondensirovannykh sredakh (Electronic Excitation Energy Transfer in Condensed Matter), Nauka, Moscow, 1978 (Eng. Transl., Elsevier, New York, 1982), Chaps. 5 & 6.

[2]V. L. Vinetskiĭ and G. A. Kholodar', Radiatsionnaya fizika poluprovodnikov (Radiation Physics of Semiconductors), Naukova dumka, Kiev, 1979, Chaps. 6 & 7.

[3]V. V. Antonov-Romanovskiĭ, Kinetika fotolyuminestsentsii kristallofosforov (Kinetics of the Photoluminescence of Phosphor Crystals), Nauka, Moscow, 1966, Chaps. 2 & 4.

[4]A. I. Burshteĭn, Usp. Fiz. Nauk **143**, 553 (1984) [Sov. Phys. Usp. **27**, 579 (1984)].

[5]H. Eyring, S. G. Lin, and S. M. Lin, *Basic Chemical Kinetics*, Wiley-Interscience, New York, 1980 (Russ. Transl., Mir. Moscow, 1983), §§9.2 & 9.3.

[6]T. R. Waite, Phys. Rev. **107**, 463 (1957).

[7]A. Suna, Phys. Rev. B **1**, 1716 (1970).

[8]O. Wilemsky and M. Fixman. J. Chem. Phys. **58**, 4009 (1973).

[9]A. I. Onipko, Fiz. Mnogochast. Sistem (Physics of Many-Particle Systems), No. 2, 60 (1982).

[10]Yu. Kh. Kalnin' and F. V. Pirogov, Preprint No. 083, LAFI, Salaspils, 1985.

[11]A. B. Doktorov and A. I. Burshteĭn, Zh. Eksp. Teor. Fiz. **68**, 1349 (1975) [Sov. Phys. JETP **41**, 671 (1975)].

[12]A. B. Doktorov, A. A. Kirpriyanov, and A. I. Burshteĭn, Zh. Eksp. Teor. Fiz. **74**, 1184 (1978) [Sov. Phys. JETP **47**, 623 (1978)].

[13]V. Kuzovkov and T. Kotomin, Phys. Status Solidi B **105**, 789 (1981); **108**, 37 (01981).

[14]A. A. Ovchinnikov, S. F. Tumashev, and A. A. Belyĭ, Kinetika diffusionno-kontrolireumykh khimicheskikh protsessov (Kinetics of Diffusion-Controlled Chemical Processes), Khimiya, Moscow, 1986.

[15]S. Chandrasekhar, "Stochastic problems in physics and astronomy," Rev. Mod. Phys. **15**, 1–89 (1943) (Russ. Transl., IIL. Moscow, 1947), Chap. 3, § 6.

[16]F. V. Pirogov and E. I. Palagishvili, Izv. Akad. Nauk Latv. SSR Ser. Fiz.-Tekh. Nauk No. 4, 46 (1984).

[17]Yu. Kh. Kalnin' and Yu. Yu. Krikis, Izv. Akad. Nauk Latv. SSR Ser. Fiz.-Tekh. Nauk No. 1, 104 (1983).

[18]A. S. Mikhailov, Phys. Lett. A **85**, 214 (1981).

[19]A. S. Mikhailov, Phys. Lett. A **85**, 427 (1981).

[20]A. S. Mikhailov and V. V. Yashin, J. Stat. Phys. **38**, 347 (1985).

[21]A. S. Mikhaĭlov and V. V. Yashin, Fiziko-khimicheskie protsessy v nizkotemperaturnoĭ plazme (Physico-Chemicl Processes in a Low-Temperature Plasma), Nauka, Moscow, 1985, p. 168.

[22]M. Doi, J. Phys. A **9**, 1465, 1479 (1976).

[23]Ya. B. Zel'dovich and A. A. Ovchinnikov, Zh. Eksp. Teor. Fiz. **74**, 1588 (1978) [Sov. Phys. JETP **47**, 829 (1978)].

[24]E. M. Lifshitz and L. P. Pitaevskiĭ, Statisticheskaya fizika, Chast' 2: Teoriya Kondensirovannogo sostoyaniya (Statistical Physics, Part 2: Theory of the Condensed State), Nauka, Moscow, 1978 (Eng. Transl., Pergamon, Oxford, 1980), Chap. 3.

[25]Ya. B. Zel'dovich and A. A. Ovchinnikov, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 588 (1977) [JETP Lett. **26**, 440 (1977)].

[26]D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).

[27]Ya. B. Zel'dovich, Elektrokhimiya **13**, 677 (1977).

[28]A. A. Ovchinnikov, and Ya. B. Zeldovech, Chem. Phys. **28**, 215 (1978).

[29]S. F. Burlatskiĭ and A. A. Ovchinnikov, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 494 (1986) [JETP Lett. **43**, 638 (1986)].

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