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M G Rudavets and A G Rudavets‡

† Laboratory of Mathematical Physics, Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Moscow region, Russia
‡ Laboratory of Quantum Systems, Institute of Energetic Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Moscow region, Russia

Abstract. A regular method of deriving the governing adiabatic Liouvillean on a lattice for a many-body system of locally and instantaneously recombining particles in reaction $A + B \to 0$ is described. When the rate U of the recombination tends to infinity, $U \to \infty$, the local reaction Liouvillean is shown to be replaced with a non-local operator involving renormalized matrix elements which are proportional to (slow) diffusive jump rates. Properties of the new Liouvillean are described. Quantum field formalism is employed.

1. Introduction

As is known, in kinetic theory initial conditions are formulated independently of governing equations. Computer simulations carried out with the aim of studying memory effects in hydrodynamics [1], chemical kinetics [2], cellular automata [3] have shown that kinetics is determined by large-scale initial density fluctuations, while small-scale noise has no essential effect. This fact has been predicted in [4] for unimolecular decay $(A \to 0)$ and by Zeldovich and Ovchinnikov [5] for bimolecular recombination $A + B \to 0$. The qualitative picture of the phenomenon is well known and consists in a separation of reactants on later stages of the reaction and localization of the latter on interfaces. Initially, fluctuations give rise only to disturbances of density around average values. As the reaction proceeds, the average densities tend to zero and fluctuation effects become predominant. The larger the fluctuation domains the larger is the diffusive relaxation time $(t \approx l^2)$, so only long-living structures survive to the later stage providing memory about the initial fluctuations level. Due to the spatial separation of the components, the frequency of the chemically active collisions is supposed to reduce more slowly than in the case of the reaction-limited mode and the total number of particles decays as $t^{-d/4}$ for dimensions $d \leqslant 4$ and as t^{-1} for $d \geqslant 4$ [2, 5].

Considerable attention has been focused on theoretical fundamentals of fluctuation kinetics at intermediate elementary reaction rates U, $0 < U < \infty$ [2, 5, 6]. To get insight into the kinetics with arbitrary U and D_σ, the diffusion coefficient of σ species, two limiting cases: $D_\sigma \to \infty$ and $U \to \infty$ should be considered. The first case presents no difficulties. If so, one is faced with the problem of investigating the regime of instantaneous reaction, $U \to \infty$, with stratification of components A and B from the very beginning (so-called strong coupling limit), while for finite U similar structures apparently occur at later stages.

An objective of this paper is to find an effective Liouvillean L_{eff} describing many-body diffusion-limited recombination (DLR) in the case of a large adiabatic parameter Γ

$$\Gamma = U/D \gg 1 \qquad D = \max\{D_\sigma\}. \tag{1}$$

In what follows, our method closely resembles the well known adiabatic elimination in the case of few degrees of freedom discussed in section 2.1. For the many-body case, a general scheme of the method based on the Dyson equation for the evolution operator is introduced in section 2.2. The scheme consists in derivation of an effective L_{eff} for $U \to \infty$ starting with phenomenological many-body Liouvillean, L, with finite U. Exact solution for the particular case of recombination transitions without diffusive jumps is presented in sections 2.3 and 2.4. The operator L_{eff} described in sections 2.6 and section 2.7 originates from renormalization of annihilation rate by elimination of fast transitions. Main properties of L_{eff} are discussed in sections 2.6 and 2.7, its quasilinearity and action in a restricted Hilbert space being especially important. The procedure is extended to annihilation of particles of a single sort. In conclusion, a generalization of the method is presented to encompass sequential reactions. A hierarchy of timescales is explicitly assumed in this case. Application of L_{eff} to deterministic treatment of kinetics is presented in a following paper to be referred to as paper II, where a transition is made from a many-body kinetics equation for probability distribution functions (PDF) to a deterministic equation for occupation numbers, $n_{\sigma i}$ (density number). This transition is correct if each cell on the lattice contains many particles of any sort [7]

$$\langle n_{\sigma i} \rangle \gg 1. \tag{2}$$

The model obeying (1) and (2) imitates the behaviour of point-like particles with a finite radius of strong recombination. It should be emphasized that the two basic components resulting from the two large parameters (1) and (2) are important for the further analysis.

2. Model formulation

2.1. Preliminary remarks

As a prelude to our derivation of an effective Liouvillean, we now start with a familiar lattice model for diffusion and recombination

$$\partial_t n_{\sigma i} = D_\sigma \Delta n_{\sigma i} - U n_{ai} n_{bi} \tag{3}$$

where Δ is a lattice Laplacian, $n_{\sigma i}$ is occupation number, $\sigma = a, b$ refers to species, i being the cell index. There exist no methods for analytical solution of (3) with arbitrary parameters D_σ and U. The reason for this is that recombination-induced changes cannot be distinguished from linear diffusion changes. As is pointed out in [5], in the case of equal diffusion coefficients, $D_a = D_b$, a linearization of the problem is possible giving a diffusion equation for excess density, $z_i = n_{ai} - n_{bi}$, to average the solution of this equation with initial Gaussian statistics of z_i ($t = 0$). An explicit solution for different diffusion coefficients is more difficult due to bilinearity in (3).

Two strongly separated timescales exist on the DLR stage: the characteristic reaction time $\tau_R \approx U^{-1}$ and the diffusive jump time $\tau_D \approx (D_\sigma)^{-1}$, with $\tau_D \gg \tau_R$. This relation enables one to classify all changes occurring in the system as fast and slow and to

reduce the number of variables describing the state of each cell by adiabatic elimination of the fast variables [8, 9]. According to this principle, the total kinetics is represented by two distinct pathways, with separated timescales, and analysed differently on different timescales. In our case, for times of the order τ_R, the diffusive degrees of freedom are 'frozen' since $D_\sigma \ll U$, and the kinetics is governed only by local recombination processes bringing the system to a local equilibrium (quasistationary) state: (i) $n_{ai}n_{bi} = 0$. In other words, the particle density of $A(B)$ equals zero in the phase $B(A)$. After the fast reaction, on large timescales the system is governed only by a slow diffusive process, the property to be looked upon as condition (ii). According to (i), the system is separated to homogeneous regions (domains) while (ii) results in diffusive redistribution within each of them. The reaction of mutual annihilation $A + B \to 0$ occurring at interfaces of domains is also limited by the rate of the diffusive jumps from their immediate neighbourhood. We stress that the kinetics inside the domains and, moreover, at the interfaces is governed by diffusive process linearly depending on density. These statements are surprising for interacting particles in the DLR system. At first sight, the interactions between particles, together with motions of interfaces caused by the process of overflow of a phase, seems to destroy the linearity of the kinetics. This, however, is not the case. It will be shown in II that motion of the interfaces is beyond the scope of the deterministic approximation. Also a contradiction will be resolved of bilinearity following from the interactions within cells, with the resulting equations being linear in the limit of infinite recombination rate U.

In any case, the question of applicability of the linear approximation should be answered on the basis of a more general approach using a many-body treatment. The following discussion will be based on adiabatic analysis, which is a suitable tool to deal with medium stratification, with the purpose of finding an *adiabatic governing operator*.

2.2. Liouvillean of the system

As is well known [7, 9], kinetics equations for density and, particularly (3) can be obtained in terms of the Markov technique of statistical mechanics based on coupled equations for many-body PDF $F(\{n_{\sigma i}\}; t)$. The operator formulation of the kinetic equations [10, 11] is more compact and effective, and based on quantization of the density field according to the same rules that are commonly used in quantum field theory [12]. In the quantum version of the theory, the Liouvillean includes diffusive and reactive terms [10, 11], i.e. $L = L_D + L_R$ where

$$L_D = \sum_{\langle i,j \rangle} (\mathcal{D}_{ij}^a a_i^+ a_j + \mathcal{D}_{ij}^b b_i^+ b_j)$$

$$L_R = U \sum_i (a_i b_i - n_{ai} n_{bi}).$$

(4)

The diffusive matrices, $\mathcal{D}_{ij}^\sigma$, are given explicitly in section 2.6. The fields a_i and b_i for A and B particles, respectively, satisfy the Bose commutation relations. For instance, for the field a_i one has

$$[a_i, a_j] = 0 \qquad [a_i^+, a_j^+] = 0 \qquad [a_i, a_j^+] = \delta_{ij}$$

besides the fields $\{a_i\}$ and $\{b_i\}$ commute. Analogy to the Bose statistics follows from the fact that the field, say $\{a_i\}$, produces an arbitrary particle number in any cell, and PDF is symmetric with respect to interchanging of particles.

The evolution of the state vector $|F(t)\rangle$ is described by the equation

$$(\partial_t - L)|F(t)\rangle = 0 \qquad \text{or } |F(t)\rangle = G(t)|F(0)\rangle. \qquad (5)$$

It is more convenient to use the Laplace transform of the evolution operator $G(t) = \exp(tL)$ which is ruled by equation

$$(\omega - L)\tilde{G} = 1. \qquad (6)$$

Below we shall use the $\tilde{}$ sign to refer to the Laplace transform with variable ω conjugated to time t. If operator L did not contain the reaction, describing only unperturbed diffusive motion, the operator $\tilde{G} = (\omega - L_D)^{-1}$ could be easily calculated in terms of diffusive modes. Then one could take into account the influence of the reaction by means of perturbation theory [10, 11]. This allows one to reproduce the Smoluchowski result [13] for effective recombination rate

$$K \approx (D_a + D_b) \qquad (7)$$

and to obtain the first concentration correction to K. Unfortunately, a diagram technique for expansion in powers of U is rather cumbersome, since coefficients at each order of concentration have to be represented with infinite series in powers of U to renormalize the reaction rate.

This situation is typical of strongly correlated systems, i.e. quickly interacting in the kinetic sense. Although some ideas of qualitative description of the distribution of particles in the DLR can be found in the theory of electron gas (spin fluctuations, spin waves and so on), a straightforward application of corresponding techniques to describe classical systems runs into difficulties. The effect of separation can be described by using operators projecting onto the subspace of non-intersecting configurations of A or B. This is done by choosing the interactions between particles, that is the reaction, as the main process. Then, by analysing the effect of the reaction, transformation can be made from the total Fock space of states to the restricted subspace of all configurations formed from single-species cells. That approach is similar to the analysis of the Hubbard model [14]. So, by choosing the weak intercell diffusive exchange of particles, L_D, as a correction to large local recombination, L_R, the Dyson equation for the evolution operator $\tilde{G}$ follows in the form

$$\tilde{G} = \tilde{G}_R + \tilde{G}_R L_D \tilde{G} \qquad \text{where } \tilde{G}_R = (\omega - L_R)^{-1}. \qquad (8)$$

The operator $\tilde{G}_R$ is diagonal in real configuration space, and related to corresponding operator $\tilde{G}_R^i$ for each cell i. The latter can be easily determined for any U, since the description of kinetics within a cell is a standard problem of a reaction-limited process in a small volume with uniform density distribution [15].

2.3. Single-cell problem

The state of a cell is given by the probability $\tilde{G}_R^i$ of finding the pair of occupation numbers $n = \{n_a, n_b\}$. The index i may be dropped here since the cell is chosen arbitrarily. The following shorthand notation will be used: $m + p = \{m_a + p, m_b + p\}$ and $\delta(m; n) = \delta(m_a, n_a)\delta(m_b, n_b)$ indicates the Kronecker delta. If the cell initially was in the precise state n then by solving equation

$$\omega \tilde{G}_R(m; n) = U[(m_a + 1)(m_b + 1)\tilde{G}_R(m + 1; n) - m_a m_b \tilde{G}_R(m; n)] + \delta(m; n) \qquad (9)$$

it can be shown that the probability of having the state $(n - p)$ at later times is performed from Laplace inversion of

$$\tilde{G}_R(n-p\,;n) = 1/[\omega + U(n_a - p)(n_b - p)]. \tag{10}$$

According to stoichiometry of the recombination, the variable p takes on integer values from 0 to $p_* = \min(n_a, n_b)$. At the end of the recombination, the cell will contain either $\{0, n_b - n_a\}$ particles in the case $n_b \geqslant n_a$, or $\{n_a - n_b, 0\}$ if $n_a \geqslant n_b$. Hence, the probability of transition to the final state is given by the expression

$$\tilde{G}_R(n - p_*, n) = \omega^{-1}. \tag{11}$$

Actually, the initial number of particles n is not well defined, and it is desirable to have for $\tilde{G}_R$ an expression that would correspond to transitions from an arbitrary initial state. This problem is simply solved in the Fock basis

$$|n\rangle = |n_a, n_b\rangle = |n_a\rangle|n_b\rangle = (a^+)^{n_a}(b^+)^{n_b}|0\rangle.$$

It is convenient to define here state $|n\rangle$ differing from that commonly used in [12] by the normalization factor. The operators $a^+(a)$ create (destroy) an A-kind state $|n_a\rangle$ according to the following rules:

$$a^+|n_a\rangle = |n_a + 1\rangle$$
$$a|n_a\rangle = n_a|n_a - 1\rangle.$$

We have defined that expansion coefficient F_n of the exact vector state $|F\rangle$ on the basis $|n\rangle$ means the probability of realization of the state $|n\rangle$. The operator $\tilde{G}_R$ is then expressed via transition operators in the Fock representation

$$\tilde{G}_R = \sum_p \sum_n |n-p\rangle(\tilde{G}_R(n-p, n)(n!)^{-1})\langle n| \tag{12}$$

where $n! = n_a!n_b!$, and $|n - p\rangle = (a^+)^{n_a - p}(b^+)^{n_b - p}|0\rangle$. Acting with the evolution operator $\tilde{G}_R$ on arbitrary initial state $|k\rangle$, one finds that, in agreement with (10), the vector $|F\rangle$ is a linear combination of the states $|k - p\rangle$ with the probabilities $\tilde{G}(k - p, k)$.

Since we are interested in the case $U \gg D$, we are clearly at liberty to choose the asymptotic value $U \to \infty$. Equation (12) is then appreciably simplified since the transition from any initial state occurs with suppressed probability to just final state. More exactly, the action with the fast reaction operator R on a mixed cell containing A and B particles, transforms it to the pure cell with component of either A or B depending on the type of particles surplus at time zero. The action with R on a single-component (pure) cell does not change its state, the empty cells can also be considered as single-component: both kinds are holes. These properties are evident from looking at the expression for $\tilde{G}_R$ in the unfolded form

$$\tilde{G}_R = \frac{1}{\omega} R \tag{13a}$$

where

$$R = \sum_{n=0}^{\infty} \left((n!)^{-2}|0\rangle\langle 0|a^n b^n + \sum_{p=1}^{\infty} \frac{1}{n!(n+p)!} \{ b^{+p}|0\rangle\langle 0|a^n b^{n+p} + a^{+p}|0\rangle\langle 0|a^{n+p} b^n \} \right). \tag{13b}$$

Here, terms with $n = 0$ represent transitions from the single-component cell. Although the form of the reaction operator R is quite complicated, it is sufficient, for our purposes, to know its action in the basis $\{|k\rangle\}$

$$R|k_a, k_b\rangle = |m_a, m_b\rangle$$

where either $m_a = 0$, $m_b = k_b - k_a$, if $k_b \geq k_a$, or $m_a = k_a - k_b$, $m_b = 0$ if $k_a \geq k_b$. It is easy to see that R is a non-Hermitian projection operator

$$R^2 = R. \tag{14}$$

This is due to the fact that only the first operator R in the left-hand side of (14) can change the state of the cell, while the second one leaves the state unchanged.

2.4. Fast reaction on a lattice

Total lattice state is determined as a product of cell states

$$|k\rangle = \prod_i |k_i\rangle \qquad \text{where } |k_i\rangle = |k_{ai}, k_{bi}\rangle = (a_i^+)^{k_{ai}}(b_i^+)^{k_{bi}}|0\rangle.$$

As before, after fast recombination of a given initial configuration has occurred, only the final configuration remains with unit probability, i.e. with probability ω^{-1} in Laplace-transform space. Hence, the following relation is fulfilled

$$\tilde{G}_R = \frac{1}{\omega} R \qquad R = \prod_i R_i \tag{15}$$

where each R_i is determined in (13b). The general structure of R can be better seen in the decomposition

$$R = \sum_{C_1} |C_F\rangle\langle C_1| \cdot \left(\prod_i \prod_\sigma k_{\sigma i}!\right)^{-1} \tag{16}$$

where $|C_1\rangle$ is an arbitrary particles' arrangement $\{k_{\sigma i}\}$, and $|C_F\rangle$ is after recombination state formed from non-intersecting configurations of particles of A and B.

2.5. Effective Liouvillean of diffusion-limited recombination

Using expression (15) for $\tilde{G}_R$, the Dyson equation (8) may be rewritten as

$$(\omega - L_{\text{eff}})\tilde{G} = R \qquad L_{\text{eff}} = RL_D. \tag{17}$$

Two important physical features are contained in this equation. Comparing it to (6), we notice that the free term, R, in (17) plays the role of an initial condition, and bilinear combination RL_D is a new Liouvillean.

It can be shown that evolution corresponding to (17) takes place not in the total Fock space but in the subspace of single-component cells. Let A and B particles at the initial time, $t = 0$, be dispersed randomly on the lattice so that in some cells both types of particle coexist together. Then after $t \approx U^{-1} = +0$ (if $U \to \infty$), the recombination destroys all less abundant particles in the mixed cells producing single-component ones. Thus at time zero plus, the state of the system will be described by the vector $|F(+0)\rangle = R|F(0)\rangle$. It corresponds to the right-hand side in (17). At later times, the total state vector will be determined by time-independent operator L_{eff}

$$|F(t)\rangle = \exp(tL_{\text{eff}})|F(+0)\rangle. \tag{18}$$

It is presented by a linear combination of terms with all possible combinations of diffusive jumps. All states of the system are generated by successive action with L_{eff} on $|F(+0)\rangle$. Each elementary act consists of a diffusive jump violating the single-component state of one of the cells followed by instant recombination restoring

homogeneous states. As a result, each state vector belongs to the subspace of non-intersecting configurations. Therefore at the DLR stage, the observed manifold is not total Fock space, in which cells may be occupied by particles of both kind, and that is realized under the conditions $\Gamma \approx 1$. In fact, it represents an 'effective' part of the space, which is formed by single-component cells only. Transitions between different configurations within this subspace are described by operator L_{eff}. The latter has the following important property: matrix elements of the L_{eff} are proportional to the coefficients D_σ because the transition rates caused by R are either unity (for transitions between states satisfying recombination stoichiometry) or zero. Hence the operator R does not bring additional factors to the rate of the elementary process. Returning to results of subsection 2.1, one concludes that L_{eff} is governing adiabatic operator determining effective observable dynamics of the system.

One may look at the action L_{eff} from the point of view of non-equilibrium thermodynamics. After fast irreversible recombination, the initial components, products, and buffer achieve an equilibrium state on each cell. From equations (14) and (18) the state vector $|F(t)\rangle$ can be represented in the form

$$\left(R + \sum_{m=1}^{\infty} (t^m/m!)(RL_D R)^m \right)|F(0)\rangle \tag{19}$$

showing that each subsequent diffusion transition displaces the system away from the equilibrium state prepared by the reaction. Hence L_{eff} determines evolution of the system in locally equilibrium conditions.

The operators R and L_D are written in different representations. The first one is presented in terms of single-site Hubbard transition operators [14]

$$X^{n,m} = |n_a, n_b\rangle\langle m_b, m_a|(m_a! m_a!)^{-1}$$

while L_D is expressed via quantization operators. There is a simple relation between R and L_D which is based on the property of completeness of the basis $\{|n\rangle\}$, i.e. $\sum_n X^{n,n} = 1$, and multiplication rules $X^{n,m}X^{N,M} = \delta(m; N)X^{n,M}$, where $|n\rangle, |m\rangle, |N\rangle, |M\rangle$ are single-site configurations. The Bose operators a, a^+ and b, b^+ can be expressed through $X^{n,m}$ to give operators R and L_D which linearly and quadratically depend on $X^{n,m}$, respectively. The total operator $L_{eff} = RL_D$, as it turns out, has simpler form when presented in terms of field operators a_i and b_i.

We postpone now derivation of L_{eff} to subsection 2.7, and discuss the DLR kinetics for two adjacent cells isolated from the rest of the lattice.

2.6. Diffusion-limited reaction for two cells

The Liouvillean of the diffusive transitions $L_D = L_D^a + L_D^b$ reads

$$L_D = \sum_i \sum_j [D_a(a_j^+ - a_i^+)a_i + D_b(b_j^+ - b_i^+)b_i] \tag{20}$$

where D_a and D_b are the rates of diffusive jumps. Particle balance between two adjacent cells i and $j = i + e$ is described by the operator in square brackets in (20). For a system with immobile A particles, $D_a = 0$, and B particles moving from i to $j = i + e$, the action of the operator

$$L_{eff}^{i \to j} = RD_b(b_j^+ b_i^+ - b_i^+ b_i^+) \tag{21}$$

depends on A particles being present in the cell j. As we know, starting with time $t = +0$, all particles on the lattice are single-component. This means that there are two

possible ways to arrange particles between the cells: (1) cell i contains B particles, $n_{bi} \geq 1$, and cell j contains A, $n_{aj} \geq 1$; (2) cell i has B and cell j has no A partiticles, $n_{aj} = 0$.

In the first case, operation with the first term $L_{\text{eff}}^{i \to j}$ in (21) on the state

$$|22\rangle = |0_{ai}, n_{bi}\rangle |n_{aj}, 0_{bj}\rangle \tag{22}$$

describes the motion of a single B particle from i to j followed by its destruction by recombination with a single A particle in j. As a result, the final state will contain one particle less in both cells than the initial state:

$$|23\rangle = D_b n_{bi} |0_{ai}, n_{bi} - 1\rangle |n_{aj} - 1, 0_{bj}\rangle. \tag{23}$$

State $|23\rangle$ could also be obtained by acting on the state $|22\rangle$ with operator

$$D_b a_j b_i \hat{n}_{aj}^{-1} \tag{24}$$

where $\hat{n}_{aj} = a_j^+ a_j$ is the 'number-of-particles' operator for A particles in the cell j. With the use of this rather peculiar operator, (24), the factor n_{aj} has dropped out of the final expression (22). The same, for instance, might be accomplished by operator $(1 + \hat{n}_{aj})^{-1} a_j$ instead of $a_j \hat{n}_{aj}^{-1}$; the results of various methods of evolution of configuration $\{n_{\sigma i}\}$ are equivalent. The second term in (21) does not change the configuration $|22\rangle$. Since the latter consists of single-component cells, the total number of particles is also preserved under action with R, i.e.

$$R D_b b_i^+ b_i = D_b b_i^+ b_i = D_b (a_j^+ a_j \cdot \hat{n}_{aj}^{-1}) b_i^+ b_i. \tag{25}$$

In the second equality in (25), the identity $(\hat{n}_{aj}/\hat{n}_{aj}) \equiv 1$ is used under the condition $n_{aj} \geq 1$. Hence, the balance of transitions in the manifold $\{|22\rangle\}$ provides the following Liouvillean which is equivalent to (21):

$$L_{\text{eff}}^{i \to j} = D_b (a_j b_i - a_j^+ a_j \cdot b_i^+ b_i) \hat{n}_{aj}^{-1} \theta(\hat{n}_{aj}) \tag{26}$$

where

$$\theta(m) = \begin{cases} 1 & m \geq 1 \\ 0 & m = 0 \end{cases} \tag{27}$$

is the characteristic (step) function in the Fock basis of occupation numbers that guarantees that equations (24) and (25) are valid in the case (1).

The second case with zero numbers of A in the cell j corresponds to the manifold of states

$$|0_{ai}, n_{bi}\rangle |0_{aj}, n_{bj}\rangle \tag{28}$$

with possible presence of B in the cell j, $n_{bj} \geq 0$. There is no recombination of particles in this case, and the right-hand side in (21) can be also expressed as

$$L_{\text{eff}}^{i \to j} = D_b (b_j^+ b_i - b_i^+ b_i) \delta(\hat{n}_{aj}). \tag{29}$$

The correlation operator presented in (29)

$$\delta(\hat{n}_{aj}) = 1 - \theta(\hat{n}_{aj}) \tag{30}$$

means that the state (28) can be changed only in the case $n_{aj} = 0$. From equations (26) and (29), we find the total Liouvillean for particles jumping from i to j

$$L_{\text{eff}}^{i \to j} = D_b (a_j b_i - a_j^+ a_j \cdot b_i^+ b_i) \cdot \hat{n}_{aj}^{-1} \theta(\hat{n}_{aj}) + D_b (b_j^+ b_i - b_i^+ b_i) \delta(\hat{n}_{aj}). \tag{31}$$

Usually, the direction of the jump is not known before-hand: from i to j or from j to i. The Liouvillean has to be written in symmetrical form to take into account both possibilities

$$L_{\text{eff}} = L_{\text{eff}}^{i \to j} + L_{\text{eff}}^{j \to i}. \tag{32}$$

Now we can predict the structure of the full two-cell Liouvillean describing transitions in the subspace of single-component cells for the case when both A and B species are mobile. It is formed with a sum of two terms analogous to Liouvillean described in (32) and symmetrical relative to permutations of the indices a and b.

2.7. *Effective Liouvillean on the whole lattice*

Now that the two-cell L_{eff} is defined, we can describe all the transitions on the lattice by making use of the fact that the total Liouvillean is given by the sum of equivalent two-cell Liouvillean, equation (32). For the B particles, we have

$$L_{\text{eff}}^b = R L_D^b = D_b \sum_{i,e} R \cdot 1 \cdot (b_{i+e}^+ - b_i^+) b_i.$$

The unit operator, 1, for each bond $(i, i+e)$ should be expressed via correlation operators $\theta(\hat{n}_{ai})$ and $\delta(\hat{n}_{ai})$ (see equation (30)) in order to account for the fate of B particles jumping to the cell $j = i + e$ depends on whether B meets A in jth cell or not

$$L_{\text{eff}}^b = D_b \sum_{i,e} [R \delta(\hat{n}_{ai+e}) \cdot (b_{i+e}^+ - b_i^+) b_i + R \theta(\hat{n}_{ai+e}) \cdot (b_{i+e}^+ - b_i^+) b_i]. \tag{33}$$

Eliminating in (33) the transition operators R by using the same bosonization procedure that has been used earlier in the two-cell problem, we obtain expression for L_{eff}^b containing only the Bose fields

$$L_{\text{eff}}^b = \sum_{i,e} (\text{RHS in (32)}). \tag{34}$$

The correlation operators θ and δ in equations (31) and (32) are in the extreme right position. It is operators θ and δ that act on the state vector first to determine the way of the transition depending on the state of the configuration: either recombination or diffusive transition.

The expression for L_{eff}^a can be obtained by relabelling $a \Leftrightarrow b$. By so doing, one finally arrives at the explicit decomposition of the total $L_{\text{eff}} = L_{\text{eff}}^a + L_{\text{eff}}^b$, i.e.

$$L_{\text{eff}} = \sum_{i,e} [D_a(b_{i+e} a_i - \hat{n}_{bi+e} \hat{n}_{ai}) \cdot \hat{n}_{bi+e}^{-1} \theta(\hat{n}_{bi+e})$$

$$+ D_b(a_{i+e} b_i - \hat{n}_{ai+e} \hat{n}_{bi}) \cdot \hat{n}_{ai+e}^{-1} \theta(\hat{n}_{ai+e})$$

$$+ D_b(b_{i+e}^+ b_i - \hat{n}_{bi}) \cdot \delta(\hat{n}_{ai+e})$$

$$+ D_a(a_{i+e}^+ a_i - \hat{n}_{ai}) \cdot \delta(\hat{n}_{bi+e})]. \tag{35}$$

To illustrate that the rate is renormalized, it is convenient to compare L_{eff} with the Liouvillean of non-local recombination in a kinetically-limited regime [10, 11]

$$L_R' = U \sum_{i,e} (a_{i+e} b_i - \hat{n}_{ai+e} \hat{n}_{bi}).$$

Since the adiabatic Liouvillean L_{eff} is proportional to the diffusion coefficients and contains no parameter U, it mathematically expresses the idea that the recombination is diffusion limited.

The four following terms in the Liouvillean (35) uniquely specify a set of transitions on the manifold of single-particle states

$$|a\rangle|b\rangle \xrightarrow{D_a} |0\rangle|0\rangle \tag{36\alpha}$$

$$|a\rangle|b\rangle \xrightarrow{D_b} |0\rangle|0\rangle \tag{36\beta}$$

$$|b\rangle|0\rangle \xrightarrow{D_b} |0\rangle|b\rangle \tag{36\gamma}$$

$$|a\rangle|0\rangle \xrightarrow{D_a} |0\rangle|a\rangle. \tag{36\delta}$$

The transition (36α) describes the jump of an A particle with rate D_a to the adjacent cell containing a B particle; the transition (36δ) expresses the jump of A to an empty adjacent cell. Jumps of B particles are reflected in the channels (36β) and (36γ). The state vector $|0\rangle$ represents state of empty cells.

Some of the properties of L_{eff} can be deduced immediately. Drop correlation operators θ and δ in (35). New Liouvillean L_{eff}^*, acting on $|F\rangle$, forms vector $|F'\rangle = L_{\text{eff}}^*|F\rangle$ linearly depending on occupation numbers of the current configuration $\{n_{\sigma i}\}$. From this point of view, L_{eff}^* is similar to diffusion operator L_D. The only effect of the reaction part of L_{eff}^* is to change arguments of the state $F(\{n_{\sigma i}\}; t)$. It will be shown in II that it is the linear factors of the vector $|F'\rangle$ rather than its arguments that result in the linear form of the kinetic equation for $n_{\sigma i}(t)$ in the deterministic approximation. Within the scope of the deterministic approximation, changings of the correlation functions do not occur. In other words, the value of $\theta(n_{\sigma i})$ for an arbitrary cell, which is either unity or zero depending on the preparation conditions, conserves as long as the criterion of deterministic approximation, equation (2), is fulfilled. The following two properties should be noted: (i) the transition rates in the balance equation for the PDF $F(\{n_{\sigma i}\}; t)$ are linear functions of the configuration $\{n_{\sigma i}\}$; (ii) in the deterministic approximation (2) the values of $\theta(n_{\sigma i}(t))$ are conserved in time; both properties may be considered as reflecting the quasilinearity of L_{eff}.

At the end of this section, let us make some generalizations and discuss how the effective Liouvillean will be modified in the case of the fields a_i and b_i obeying Pauli statistics [11]

$$c_{\sigma i}^2 = c_{\sigma i}^{+2} = 0 \qquad \text{for } i = j, \text{ where } c_{ai} = a_i, \, c_{bi} = b_i$$

$$[c_{\sigma i}, c_{\sigma j}] = [c_{\sigma i}^+, c_{\sigma j}^+] = [c_{\sigma i}, c_{\sigma j}^+] = 0 \qquad \text{for } i \ne j. \tag{37}$$

The fields a_i and b_i are assumed to be independent, so that mixed cells would occur. Firstly, we notice that the scheme of the Liouvillean derivation obtained for the Bose statistics remains true for the Pauli case. It can be easily checked that the reaction operator for each cell equals $R_i = 1 - \hat{n}_{ai}\hat{n}_{bi} + a_i b_i$, since it obeys the following equalities $R|ab\rangle = |0\rangle$, $R|a\rangle = |a\rangle$, $R|b\rangle = |b\rangle$, $R|0\rangle = |0\rangle$. Inasmuch as the occupation numbers are bounded to $n_{\sigma i} = 0, 1$, the correlation operators are simplified to

$$\theta(\hat{n}_{\sigma i}) = \hat{n}_{\sigma i} \qquad \delta(\hat{n}_{\sigma i}) = 1 - \hat{n}_{\sigma i}.$$

As a result, the effective Liouvillean is given by

$$L_{\text{eff}} = \sum_{i,e} [(D_a + D_b)(a_{i+e}b_i - \hat{n}_{ai+e}\hat{n}_{bi})$$

$$+ D_b(b_{i+e}^+ - b_i^+)b_i(1 - \hat{n}_{ai+e}) + D_a(a_{i+e}^+ - a_i^+)a_i(1 - \hat{n}_{bi+e})]. \tag{38}$$

According to (38), an A particle jumps with the rate D_a from ith cell to the adjacent cell $j = i + e$ when there is no B particle there, $n_{bj} = 0$, all particles in the system being conserved in this case. If there is a B particle in the jth cell, annihilation happens at the rate of the mutual diffusion coefficient $(D_a + D_b)$.

An additional comment can be made on the relation between the DLR and a single-species annihilation $A + A \rightarrow 0$. Construction of the effective Liouvillean follows the same procedure as explained above, giving the final result

$$L_{\text{eff}} = 2D_a \sum_{i,e} [(1 - a^+_{i+e} a^+_i) a_{i+e} a_i \cdot \hat{n}_{ai+e} + (a^+_{i+e} - a^+_i) a_i \cdot (1 - \hat{n}_{ai+e})]. \quad (39)$$

Making use of the identities $a_i \hat{n}_{ai} = a_i$, $a^{+2}_i = 0$, equation (39) is simplified and written in the form of bilinear operator [16]

$$L_{\text{eff}} = 2D_a \sum_{i,e} (a^+_{i+e} - a^+_i + a_{i+e}) a_i. \quad (40)$$

The operator (40) for one-dimensional diffusion can be diagonalized, permitting one to obtain the precise solution for the total particle number ($\approx t^{-1/2}$) at later stages of the reaction [16, 17].

3. Summary and discussion

A regular method of derivation of adiabatic Liouvillean for a many-body system with fast recombination is proposed. The method presents a statistical analogue of the technique of adiabatic elimination of fast variables in the theory of Brownian motion [8, 9], chemical kinetics [18], and stochastic systems [9]. The cornerstone assumption of the method is the essential difference between recombination and diffusive rates

$$U \gg D \qquad \text{where } D = \max\{D_\sigma\}.$$

It is this situation which takes place in the DLR. The inequality implies separation of timescales, i.e. $\tau_R = 1/U \ll \tau_D = 1/D$ and, hence, distinction of recombinative and diffusive pathways. In the recombinative channel which is favoured at the initial stage, the particles rapidly and locally recombine according to the evolution operator R stated explicitly in (16). The diffusive pathway is unaffected on the timescale τ_R and is quenched after a delay of the order τ_D. The main features of the DLR kinetics are presented in the infinite U model, for which the net result of both channels leads to effective dynamics with the many-body Liouvillean $L_{\text{eff}} = RL_D$ on the manifold of single-component states. The kinetics is governed by the slow operator proportional to the coefficients D_σ, equation (35).

Guided by our experience with a single reaction, we can guess L_{eff} for problems involving a sequence of several reactions. Suppose that the reaction rates U_ρ form a hierarchy of scales, jumps being the slowest process

$$U_S \gg U_{S-1} \gg \ldots \gg U_1 \gg D.$$

This implies the hierarchy of timescales, $\tau_\rho = U_\rho^{-1}$, where $\rho = 1, 2, \ldots, S$, i.e.

$$\tau_S \ll \tau_{S-1} \ll \ldots \ll \tau_1 \ll \tau_D.$$

Analysis of the system obeying the hierarchy begins with the fastest reaction occurring with the rate U_S, while all other processes with larger relaxation time are 'frozen'. An initial point of the elapsed time is chosen arbitrarily, then after time τ_S the products

of the Sth reaction take part in the following reaction, $\rho = S - 1$, on the interval of time $\tau_S < t < \tau_S + \tau_{S-1}$. Products of the latter reaction react over the next time interval τ_{S-2} with rate U_{S-2}, and so on. Having ordered the interactions, we removed the necessity for describing all intermediate transitions on the timescale τ_D and eliminated a considerable number of the internal degrees of freedom. For each reaction ρ, it is sufficient to know just the initial state of the components resulting from the previous reaction $(\rho - 1)$ and the final state, which is assumed to be unique in the Fock basis. The analysis is correct if each product emerges only once in the chemical scheme of local reactions—no autocatalytic reactions. Denoting the operator of reaction in the ρ channel as R_ρ, the total adiabatic Liouvillean that describe the evolution at scales τ_D is given by

$$L_{\text{eff}} = R_{\text{eff}} L_D$$

where $R_{\text{eff}} = R_S R_{S-1} \ldots R_1$ represents the net result of all reactions, each R_ρ has a form analogous to that given by (16). Application of the general adiabatic analysis is also possible to chemical kinetics [7, 18], and hydrodynamics with a discrete velocity set [7, 11, 19]. The Liouvillean for the latter system closely resembles the Hamiltonian for multiband Hubbard-like models with a number of orbitals strongly coupled on sites.

At the end of this section, we re-examine the recombination operator for the two-species system. It has been shown that the bosonization tool enables one to express the operator $R L_D$ in terms of the correlation operators $\theta(\hat{n}_{\sigma i})$ and $\delta(\hat{n}_{\sigma i})$. The trigger function of these operators is in choosing the way of changing the current state, i.e. either diffusive pathway of molecules (jumps) or recombinative pathway (jumps + annihilation). The Liouvillean L_{eff} provides the model for many-body analysis of the instantaneous recombination. However, it seems not to be exactly solvable, so deterministic approximation of kinetic equations that correspond to L_{eff} will be derived and discussed in II.

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