Pairing correlations in diffusion-limited recombination: coupled-cluster study in Fock space

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Abstract. The purpose of the paper is to illustate how the cluster method, introduced originally in classical statistical mechanics and later on generalized to describe correlation effects in quantum systems, can be extended for treating collective behaviour in diffusion limited recombination $A + B \rightarrow 0$. This involves exploring a many-body state vector in second quantization form with pairing correlations between particles only. An algebraic approach for deriving kinetics equations for pair correlation functions $g_{\lambda\lambda'}(r, t)$ is proposed, where $\lambda, \lambda' = a, b$. Solution of those equations is presented. In two-body approximation, $g_{ab}(r, t)$ and the corresponding time-dependent rate constant reproduce the Smoluchowski results. Many-body effects are analysed both for a monomolecular regime ($c_b \gg c_a(t)$) (MR) and a bimolecular regime ($c_b(t) = c_a(t)$) (BR). For MR at $c_b \rightarrow 0$, $g_{ab}(r, t)$ is shown to have exponential screening on the characteristic length inversely propotional to $\sqrt{c_b}$, and the rate constant acquires additional correction, proportional to $\sqrt{c_b}$, to the Smoluchowski value. For BR at the later stage of recombination, the pair correlation function is predominantly determined by the initial condition, i.e. $g_{ab}(r, 0)$, and the average concentration c_a is found to exhibit time dependence $\approx t^{-3/4}$ at the pre-asymptotic stage. However, at the true asymptotic, $t \rightarrow \infty$, the model gives $c_a \approx t^{-1}$. We confront these results with the previous analytical results and find a qualitative consistency in the MR case and some discrepancy for the BR case. The proposed description is rather simple and can be applied for exploring collective and correlation effects in other non-equilibrium classical systems.

1. Introduction

It has become increasingly clear that theoretical description of diffusion-limited recombination $A + B \rightarrow 0$ (DLR) poses a problem of fundamental interest in its own right [1–17]. DLR is an example of a many-body system showing spontaneous stratificaton of reagents followed by slowing of kinetics. Most studies of this phenomena have been discussed in the context of the statistical justification of the temporary decay of the concentration $c \approx t^{-d/4}$ (d is the dimension of space), that has been theoretically predicted in [2] and later on observed in computer simulations [3], and also the extension of the theory [2] for parallel reactions [4, 5]. Theoretical approaches to DLR make use of all available techniques of many-body physics. A fairly good agreement with [2, 3] has been achieved by several methods: Kirkwood approximation [9–11], decoupling techniques [12] and field theoretical approaches [13, 14].

It is now common to distinguish two stages in DLR: the initial stage and the asymptotic stage.

(a) At the initial stage of recombination, the typical configurations of reagents can be viewed as a mixture of a vast number of small homogeneous domains dispersed randomly among relatively large conglomerates. Collective processes, here, modify the two-body effective rate of recombination, making it concentration dependent.

(b) At the asymptotic stage of DLR, the small size domains recombine, so that recombination localizes at the interface of the surviving homogeneous conglomerates. Accompanied kinetics proceeds slower than $c(t) \approx t^{-1}$. That is the fluctuation regime of DLR, described by the law $c \approx t^{-d/4}$.

Statistical justification of the fluctuation regime is rather a challenging task, and is not the subject of this paper. Instead, keeping in mind problem (b), we direct our attention to the initial stage of DLR. More precisely, the aim is to describe the influence of pairing correlations on the kinetics of DLR. The possibility for this study stems from cluster ideas [18] about the role of pairing correlations in electron gas. The present work has been inspired by the second quantization version of the cluster expansion method, usually referred to as the coupled cluster approach (CCA); for a comprehensive review and guide to the literature see [19–21]. The advantage of the CCA is three-fold. First, the CCA automatically takes into account the indistinguishability of classical particles when the Bose statistics for creation and annihilation operators of particles is chosen, thereby providing an algebraic technique for description of the systems. Second, it permits, selectively, sum ladder, ring, and other diagrams without requiring perturbation analysis. This is an appealing point, since the ring diagrams, or in other words, terms responsible for random phase approximation (RPA) help substantially in understanding microscopically the occurrence of collective modes in many-body systems [22]. And last, but by no means least, it treats on an equal footing both closed and open systems in which the particle numbers irreversibly change during the course of the reaction, and all the processes are governed by a non-Hermitian Liouvillean. We eschew a variational description of DLR owing to the lack of Hermicity of the Liouvillean. It is the projective (non-variational) character of the CCA that allows us to adopt CCA for inquiring into DLR.

At first sight, the collective description is applicable to long-range interactions between particles. Indeed, for the collective behaviour to be valid a test particle must be affected simultaneously by many other particles of the system. In DLR, the role of long-range interactions is played by the two-body correlation function of the Smoluchowski approximation, that behaves as $g_{ab}(r, t) \approx r^{-1}$ at $r \to \infty$ and $t \to \infty$, while elemenary rates of pair recombination is of short range in space. The long-range character of $g_{ab}(r, t)$ suggests the occurence of long-range drift $J = -D\nabla g_{ab}$ towards the region exhausted of diffused particles. One should therefore account for the kinetics of the many-body distribution function by considering the two-body function.

In the present paper, we report an extension of the CCA to non-equilibrium classical systems incorporating irreversible rapid recombination. To do this, we first write out the full distribution function $F(x, t)$ (DF) in terms of the Prigogine–Balescu expansion and transform it to second quantization form, $|F\rangle$. In section 3, a general scheme of time-dependent CCA for reacting systems is constructed; in particular, we emphasize the role of pairings between particles. A relation between the CCA state vector and the Prigogine–Balescu state vector is given in section 4. The main idea of the CCA is in guessing the exponential form of vector state $|F\rangle$ in a prescribed manifold of states. So, the results obtained are clearly dependent on *a priori* suggestions concerning $|F\rangle$. A justification for pairing correlation approximation, which we adopt for DLR in section 5, is based on the utility of this approximation in treating correlation

properties in homogeneous electron systems as well as for atoms and molecules. Kinetics equations for average concentrations of particles and for pair correlation functions $g_{\lambda\lambda}(r, t)$, where $\lambda, \lambda' = a, b$, will be obtained, relying on the algebraic approach of sections 6 and 7. Solution to these equations is examined in section 8 in two-body approximation. This is followed by analysis of the full equations involving a collective description in section 9. Section 10 summarizes the major conclusions of the calculations and outlines the extension of the theory. Finally, in the appendices we list useful formulae used in this paper.

2. Representation of state vector in Fock space

Particle concentration, from a statistical point of view, is determined via reduced DF. A regular method to gain knowledge about the reduced DF is provided by Prigogine–Balescu expansion of the full DF. We begin by reviewing briefly some basic facts on this subject. Our purpose is to constuct the second quantization representation for the expansion of $|F\rangle$.

Write out the full DF for n particles on a lattice with Ω cells as a multiple Fourier expansion [23, 24]

$$F^{(n)}(x, t) = \Omega^{-n} \sum_{(k)} \Phi^{(n)}(k, t) \sum_{p} \exp\left(-i \sum_{j=1}^{n} k_j x_{pj}\right). \tag{1}$$

On labelling each particle, $F^{(n)}(x, t)$ specifies the probability of finding n particles in the configuration $x = (x_1, \ldots, x_n)$, with j's argument meaning the coordinate of the cell containing particle number j. The symmetry of $F^{(n)}(x, t)$ relative to the interchange of labels is provided by summing all possible permutations, p, of labels. The function $\Phi^{(n)}(k, t)$ is symmetric in the Fourier k-space. The wavevectors k_j take over the first Brillouin zone of a simple cubic lattice. Throughout the paper, we assume DLR on a three-dimensional lattice, and use letters k, q to specify functions in the Fourier space and letters r, x to denote coordinate representation.

In order to determine the expected values from (1), one needs to expand this series in terms of particle numbers with zero wavevector [23, 24]

$$F^{(n)}(x, t) = \Omega^{-n}\left(\phi_0(t) + \sum_{k}' \phi_1(k, t) \sum_{j=1}^{n} \exp(-ikx_j)\right.$$

$$\left. + \sum_{k_1, k_2}' \phi_2(k_1, k_2, t) \sum_{i \neq j}^{n} \exp(-ik_1 x_i - ik_2 x_i) + \ldots\right). \tag{2}$$

Here and in the following, the prime over the sum signifies that the state with $k = 0$ is excluded. The reduced distribution function $\phi_0(n, t) = \Phi^{(n)}(0, t)$ denotes the probability of finding n particles in the system. When a reaction occurs, the n is a stochastic variable, so the normalization condition

$$\sum_{n=0}^{\infty} \phi_0(n, t) = \sum_{n=0}^{\infty} \sum_{(x)}^{\infty} F^{(n)}(x, t) = 1 \tag{3}$$

should be fulfilled. If we are thinking of ϕ_0 as an intensive variable, the function $F^{(n)}$ should be of order $\Omega^{-n}O(1)$. In general, extraction of volume-dependence in reduced

DF, as will be shown in section 7, is a decisive condition for choosing the 'right' variables for description of the many-body system. The next reduced DF is one-body DF, $\phi_1(k) = \Phi^{(n)}(k, 0 \ldots 0)$, which can be easily found by the Fourier transformation (2), and has order $\Omega^{-1}O(1)$. For statistically homogeneous systems, which we are interested in, the $\phi_1(k) = 0$ identically. The two-body DF, $\phi_2(k, -k) = \Phi^{(n)}(k, -k, 0, \ldots, 0)$ can be found by multiple summation of (1) over all configurations $x' = (x_3, \ldots, x_n)$ for $(n-2)$ particles

$$f_2(r, t) = \Omega^{-2}\left(\phi_0(t) + \sum_k{}' \phi_2(k, -k, t) \exp{(ikr)}\right) \tag{4}$$

where $f_2(x_1 - x_2, t) = \Sigma_{(x')} F^{(n)}(x, t)$, with $r = x_1 - x_2$. Since function f_2 is of the order $\Omega^{-2}O(1)$, so from (4), it follows that $\phi_2(k, -k, t)$ is of the order $\Omega^{-1}O(1)$. The contracted description of the whole system is seen to be built into Fourier transformed DF, $\Phi^{(n)}(k, t)$, containing nearly all particles with mode $k = 0$.

Having fixed notations, the discussion now proceeds to the second quantizide representation [22] rather than the coordinate one. Just as for the wavefunction for Bose particles in quantum mechanics, the DF $F^{(n)}(x, t)$ is symmetric relative to the interchange of particle labels [25]. So, in accordance with the quantum mechanical 'recipe', by choosing a set of 'occupied' states k_i, we can assign each particle to a state k and, thus, associate a combination

$$\Omega^{-n} \sum_p \exp\left(-i \sum_{j=1}^n k_j x_{pj}\right)$$

with shorthand notation

$$\prod_{j=1}^n a_{k_j}^+ |0\rangle.$$

Here $|0\rangle$ is vacuum of particles, operator a_k^+ adds a new state k, while operator a_k removes it from the many-body state. By allowing these operators to obey the Bose commutation relations

$$[a_k, a_q] = 0 \qquad [a_k^+, a_q^+] = 0 \qquad [a_k, a_q^+] = \delta(k - q) \tag{5}$$

where δ is the Kronecker delta, we provide the symmetry of the full DF in coordinate representation (1). The state (1) will now be characterised by vector

$$|F^{(n)}(t)\rangle = \sum_{(k)} \Phi^{(n)}(k, t) \prod_{i=1}^n a_{k_i}^+ |0\rangle. \tag{6}$$

It is convenient to term the one-particle state $k = 0$, which represents uniform distribution of one-particle probability, a ground state. The state when all particles have $k = 0$ will be referred to as a condensate [26]. Creation operator a_k^+ excites the condensate and gives rise to spatial inhomogeneity with wavevector k. The definitions for condensate and excitations can be applied in the Fock basis by expansion $|F^{(n)}(t)\rangle$ in powers of creation operator numbers with zero mode, employing the symmetry property of $\Phi^{(n)}$, i.e.

$$|F^{(n)}(t)\rangle = \left(\phi_0(t) + \sum_k{}' \phi_1(k, t) Q_{ak}^+ + \sum_{k_1, k_2}{}' \phi_2(k_1, k_2, t) Q_{ak_1}^+ Q_{ak_2}^+ + \ldots\right)(a_0^+)^n |0\rangle. \tag{7}$$

Single-particle excitation operators $Q_{ak}^+ = a_k^+ a_0$ and complex conjugated operators $Q_{ak} = a_k a_0^+$ are fundamental units in the Fock space. The formula (7) can be rewritten in a more explicit, but somewhat unwieldy, form by making use of identity $a_0(a_0^+)^n |0\rangle = n(a_0^+)^{n-1}|0\rangle$. The component of $|F^{(n)}(t)\rangle$ referred to as condensate, i.e. $\phi_0(a_0^+)^n|0\rangle$, defines the probability of having n particles on the lattice. The spatially non-uniform arrangement of particles is accounted for by the superposition of states with one-particle excitation only; analogously, pair distribution is included by super-position of states with two-particle excitations of condensate, and so on.

We close this section with the extension (7) applied to states of statistically homogeneous systems composed of A and B particles, namely

$$|F(t)\rangle = \left(\phi_0 + \sideset{}{'}\sum_k \phi_{aa}(-k, k, t) Q_{a-k}^+ Q_{ak}^+ + \sideset{}{'}\sum_k \phi_{bb}(-k, k, t) Q_{b-k}^+ Q_{bk}^+ \right.$$

$$\left. + \sideset{}{'}\sum_k \phi_{ab}(-k, k, t) Q_{a-k}^+ Q_{bk}^+ + \dots \right) (a_0^+)^{n_a} (b_0^+)^{n_b} |0\rangle \qquad (8)$$

where $Q_{bk}^+ = b_k^+ b_0$. The operators for A and B particles commute with each other. In (8), just as in (7), the function ϕ_0 has order $O(1)$, components $\phi_{\lambda\lambda'}$ have order $\Omega^{-1}O(1)$. In general, an order to Ω for the reduced DF coincides, up to the choice of the sign, with a number of summations over wavevectors in the corresponding term of the full $|F\rangle$. This is the so-called regularity principle for the DF [24].

3. Vector state of the CCA

The form of the state vector (8) is correct, but is awkward. It should be discarded in favour of a different (CCA) representation for $|F\rangle$ which is more convenient in practical calculations.

The state $|F\rangle$ obeys the kinetics equation [25]

$$(\partial_t - L)|F(t)\rangle = 0 \qquad \text{or} \qquad |F(t)\rangle = e^{Lt}|F(0)\rangle \qquad (9)$$

where Liouvillean, L, governing the recombination and diffusion, reads $L = L_D + L_R$, with

$$L_D = -\sum_k D_{ak} a_k^+ a_k - \sum_k D_{bk} b_k^+ b_k \qquad (10a)$$

$$L_R = \Omega^{-1} \sum_k w_k a_k b_{-k} - \Omega^{-1} \sum_{kqk'} w_q a_{k+q}^+ b_{k'-q}^+ a_k b_{k'}. \qquad (10b)$$

Here

$$D_{\lambda k} = 2D_\lambda \sum_{i=1}^{3} (1 - \cos k_i)$$

is the dispersion law for particles of $\lambda(=a, b)$ kind, D_λ is the diffusion rate, and w_k specifies the Fourier component of the rate of two-body recombination. Relying on (9) and (10), it is possible to find the reduced DF approximately by involving the projection opeator technique with subsequent implementation in perturbation theory.

To gain a correct result in the direct way one needs to sum an infinite set of terms in perturbation theory in powers of L_R. One method to meet the challenge of the summation problem is in exploring the m particle T-matrix. Practically, it is difficult to depart from the two-particle T-matrix.

Another way exists, that also differs from inductive construction of the kinetics equations; the coupled cluster approach, previously applied for calculating the correlation energy of the ground state of electron gas [19–21, 27, 28] and in time-dependent quantum systems as well [33]. This method will be adopted to the kinetical sense of our problem and will permit us to calculate, in a systematic manner, correlation properties of many-body reacting systems, at least in the lowest approximation.

A key idea of the CCA is to choose the state vector in a prescribed subspace of states. We are free to take $|F(t)\rangle$ in the form

$$|F(t)\rangle = \exp(S(t))|\Psi(t)\rangle. \tag{11}$$

The choice of the operator $S(t)$, responsible for correlation effects, and reference state $|\Psi(t)\rangle$ are cornerstones in the derivation of kinetics equations. Classification of states in $|F(t)\rangle$ as those formed from condensate by excitation of particles suggests that $|\Psi(t)\rangle$ describes the condensate state with a variable number of particles. Its form is guessed from the Liouvillean (10) by retaining operators with zero mode

$$|\Psi(t)\rangle = \exp(S_0(t))|n\rangle \tag{12a}$$

where

$$S_0 = \Omega^{-1}\gamma(t)Q_0^+ \qquad \text{and} \quad Q_0^+ = (a_0 b_0 - a_0^+ b_0^+ a_0 b_0). \tag{12b}$$

The function $\gamma(t)$ has to be determined. The vector $|n\rangle$ represents the condensate with a Poisson distribution of particles among the cells of the lattice

$$|n\rangle = (a_0^+)^{n_a}(b_0^+)^{n_b}|0\rangle. \tag{13}$$

Excitations of condensate $|\Psi(t)\rangle$ are made with $S(t)$ and make the distribution of the particles spatially inhomogeneous. Excitation operator Q_m^+ of the order m removes m particles from the condensate and simultaneously creates them in different excited states. Explicit forms of the first five operators of Q_m^+ are

$$a_k^+ a_0 \qquad b_k^+ b_0 \qquad (a_k^+ a_0)a_q^+ a_0 \qquad (a_k^+ a_0)b_q^+ b_0 \qquad (b_k^+ b_0)b_q^+ b_0. \tag{14}$$

Having ordered operators Q_m^+, we can construct the full $S(t)$

$$S(t) = \sum_m^{\text{exc}} S_m(t) \tag{15}$$

where cluster operators $S_m(t) = \sigma_m(t) Q_m^+$, and subscript m designates excited states. The first terms of expansion of $S(t)$, which are linear in $Q_{\lambda k}^+$ ($\lambda = a, b$), are as follows

$$S_a(t) = \sum{}' \sigma_a(k, t) Q_{ak}^+ \qquad S_b(t) = \sum{}' \sigma_b(k, t) Q_{bk}^+ \qquad (16a)$$

and bilinear terms read in statistically homogeneous systems as

$$S_{aa}(t) = \sum{}' \sigma_{aa}(k, t)\, Q_{ak}^+ Q_{a-k}^+$$

$$S_{ab}(t) = \sum{}' \sigma_{ab}(k, t)\, Q_{ak}^+ Q_{b-k}^+ \qquad (16b)$$

$$S_{bb}(t) = \sum{}' \sigma_{bb}(k, t)\, Q_{bk}^+ Q_{b-k}^+.$$

Temporary dependence of $S(t)$ is determined through cluster functions $\sigma_m(t)$. In analogy with (16), we can construct excitation operators of higher orders. As a result, the function $|F(t)\rangle$ will satisfy conservation of normalization (3), i.e.

$$\langle z | F(t)\rangle = \sum_n \sum_{(k)} \Phi^{(n)}(0) = 1 \qquad (17)$$

where vector

$$\langle z| = \langle 0 | \exp(a_0 + b_0) \qquad (18)$$

provides full statistical averaging over configurations and over particle numbers. Equation (17) follows from identity $\langle z | S_m = 0$, which is true for all types of indexes m. In particular, evolution of the condensate state $|\Psi(t)\rangle$ conserves normalization (17), i.e. $\langle z | \Psi(t)\rangle = 1$, for any $\gamma(t)$, once $\langle z | n\rangle = 1$ holds.

If we leave open the fact that the full set of operators S_m, with $m \geqslant 1$, generates a full space of states that is orthogonal to condensate $|\Psi\rangle$, does not change particle numbers and conserves normalization of $|F\rangle$, otherwise, we can think of the other Q_m^+. For instance, we can expand operators other than in a plane wave basis. The choice of basis depends on the symmetry of L, general properties of the arrangement of particles in the exact $|F(t)\rangle$ and the ease with which it promises an answer.

In a regular theory, a set of Q_m^+, $m \geqslant 1$, constitutes the complete and orthogonal set of excited states, i.e.

$$1 = \sum_n (|n\rangle\langle n| + \sum_m Q_m^+ |n\rangle\langle n| Q_m) \qquad (19a)$$

$$[Q_m^+, Q_{m'}^+] = 0 \qquad \langle n | Q_m^+ Q_{m'} | n\rangle = 0 \qquad m \neq m' \qquad (19b)$$

$$\langle n | Q_m = 0 \qquad (19c)$$

where $|n\rangle$ is the orthonormal zero mode condensate state.

Here, we break off from the general discussion to say a few words after [19] in favour of an exponential ansatz (11), as the formalism seems not to have been used in non-equilibrium classical kinetics before. (1) Since the cluster operators S_m are independent, the corresponding state vector factorizes as it should for probability of

independent states. (2) As a corollary of (1), the exponential ansatz (11) provides a correct dependence of expectation values on volume, Ω, and particle number, n, for arbitrary decoupling of the set $S_m(t)$, the so-called size consistency condition. Thus, one should not worry about the thermodynamic limit. (3) By Taylor expansion of the exponent, each cluster state can be represented by an infinite linear combination of states with arbitrary particle interactions inside and outside the cluster. This property corresponds to infinite summation of diagrams and effectively exlcudes divergences inherent in the usual perturbation theory. (4) A desirable set of kinetics equations for cluster functions is formed by projection of the governing equation (9) (in which $|F\rangle$ satisfies (11)) onto the complete set of states $\{\langle C|, \langle C|Q_m\}$, where $\langle C|$ is the condensate state. Physically, projection means the statistical averaging of kinetics equations over all configurations and numbers of particles. We remark that this approach applies equally to both Hermitian and non-Hermitian governing operators, the latter class including Liouvillean (10). Thus, we avoid the spectral problem in solving (9).

4. Relationship between cluster and reduced DF

There is one-to-one association between ϕ_m and σ_m. It is established in the same way as the relationship between the moments and the cumulants in classical probability theory [34]. Indeed, the full state $|F\rangle$ is expressed in terms of linear combinations of configurations, (8), and in factorized form, (11), hence

$$|F\rangle = \left(1 + \sum_m \phi_m Q_m^+\right)|\Psi\rangle = \exp\left(\sum_m \sigma_m Q_m^+\right)|\Psi\rangle. \tag{20}$$

On projecting this relationship onto the excited states, we connect ϕ_m with σ_m. For instance

$$\sigma_a(k, t) = \phi_a(k, t)/\phi_0(n, t). \tag{21}$$

This can be seen by comparison of matrix element $M = \langle n|Q_{ak}|F(t)\rangle$, when the vector $|F(t)\rangle$ is picked out in form (8) and in form (11). In writing (21), we have also used the statement

$$|\Psi(t)\rangle = \sum_n \phi_0(n, t)|n\rangle \tag{22}$$

since the normalization of $|F\rangle$ can be ascribed entirely to the condensate state $|\Psi(t)\rangle$. Analogous calculations of matrix element $\langle n|Q_{ak}Q_{a-k}|F(t)\rangle$ yield the pair cluster function

$$\sigma_{ab}(k, t) = \phi_{ab}(-k, k, t)/\phi_0(n, t). \tag{23}$$

From section 2, the regularity property of the reduced DF requires the function ϕ_{ab} to be of order $\Omega^{-1}O(1)$. This allows the solution for $\sigma_{ab}(k, t)$ to be written as

$$\sigma_{ab}(k, t) = \Omega^{-1}g_{ab}(k, t) \tag{24}$$

where we have defined the intensive function $g_{ab}(k, t)$ ($= O(1)$) which we refer to as a pair correlation function. The sense of this substitution will become clear in sections 8 and 9 where concrete calculations will be done.

If we set m-particle cluster functions σ_m with $m \geqslant 2$ to zero, then $\Phi^{(n)}(k)$ factorizes exactly

$$\Phi^{(n)}(k) \propto \prod_{i=1}^{n_a} \prod_{j=1}^{n_b} \sigma_a(k_i)\sigma_b(k_j). \tag{25}$$

So, the σ_m for $m \geqslant 2$ are responsible for correlation effects in the system.

Another property of (20) follows if we consider, for simplicity, the system composed of particles of a single kind, and restrict our analysis with S in form

$$\frac{1}{2} \sum{}' \sigma(k_1, k_2) Q_{ak_1}^+ Q_{ak_2}^+ \tag{26}$$

then the four-particle DF is seen to be

$$\phi(k_1, k_2, k_3, k_4)/\phi_0 = 2 \sum_p \sigma(k_1, k_i)\sigma(k_j, k_l).$$

Here, the sum is over all permutations, p, of different indices i, j, l, taking on values 2, 3, 4.

In order to highlight the difference between the two forms of $|F\rangle$, we emphasize that pairing correlation model (26) accounts for the kinetics of many-body DF, including ϕ_m with $m \geqslant 2$, not merely the two-body kinetics for ϕ_2. For instance, the single term $S = \sigma_{ab}(k, t) Q_{ak}^+ Q_{b-k}^+$ generates an infinite linear combination of states which can be viewed as excited from zero state condensate by operator $(Q_{ak}^+ Q_{b-k}^+)^m$, $m \geqslant 2$. The aforementioned operator S accounts for RPA.

In conclusion, the cluster functions σ_m provide contracted descriptions of many-body systems in CCA just as the set of reduced DF ϕ_m does in Prigogine–Balescu formalism. In classical many-body problems in coordinate space, the connection was known long ago [35]. We state it in Fock space now. The CCA formalism seems to provide a more suitable tool for reduction of degrees of freedom than the tranditional one.

5. Operator equation for $S(t)$ and $S_0(t)$

Once the state vector is written in the form (11), we encounter the question of how to determine the cluster functions $\sigma_m(t)$ and $\gamma(t)$. The vector

$$|F(t)\rangle = \exp(S(t)) \exp(S_0(t))|n\rangle \tag{27}$$

is an exact state fulfilling (9) when $S(t)$ generates all possible configurations of particles. So, in order to obtain the kinetics equation for $S(t)$, all we need is to perform the time derivative

$$\partial_t e^{S(t)} = \partial_t \prod_{m>0} e^{\sigma_m(t)Q_m^+} = e^{S(t)}\partial_t S. \tag{28}$$

Here, the exponent breaks into parts corresponding to different independent modes Q_m^+ (19). Then, on operating on both sides of (9) with operator $\exp(-S(t))$, we find

$$\partial_t (S + S_0) | \Psi(t) \rangle = \check{L} | \Psi(t) \rangle \tag{29}$$

where $\check{L}$ defines canonical transformation

$$\check{L} = e^{-S} L \, e^S. \tag{30}$$

Now, it only remains to carry out the projection (29) onto set $\langle C |$, $\langle C | Q_m$ to derive the kinetics equations for $\gamma(t)$ and $\sigma_m(t)$.

It is pertinent to note that if a general mathematical structure of operators L and Q_m^+ were such that they comprise a close Lie algebra, then we could find an exact set of kinetics equations for $\gamma(t)$ and $\sigma_m(t)$, as is done in the Wei–Norman algebraic procedure [36]. This is why we prefer to utilize the time-dependent formalism in treating the DLR.

6. Action mass law for $A + B \rightarrow 0$ reaction

We want to connect the cluster function $\gamma(t)$ with the average number of particles of (say) A kind, defined as

$$\langle n_a(t) \rangle = \sum_n n_a \phi_0(n_a, n_b, t) \tag{31}$$

or

$$\langle n_a(t) \rangle = \langle z | \sum_k a_k^+ a_k | F(t) \rangle = \langle z | a_0 | \Psi(t) \rangle. \tag{32}$$

As is seen, the average number of particles is determined by the condensate part of the full vector state $| F(t) \rangle$. The kinetics equation for $\langle n_a(t) \rangle$ follows immediately from the explicit form of $| \Psi \rangle$, (12), and gives the action mass law with effective rate of recombination $\dot{\gamma}(t)$, i.e.

$$\partial_t \langle n_a(t) \rangle = - \Omega^{-1} \dot{\gamma}(t) \langle n_a(t) \rangle \langle n_b(t) \rangle \tag{33}$$

(the overdot denotes the time derivative). In obtaining this result, the Bose commutation relation for zero mode has been used first, and passage to the thermodynamic limit has been done after all necessary calculations, assuming the fluctuations of the total particle number are negligible.

For a rough estimate of the function $\gamma(t)$, we suppose that mode coupling in Liouvillean L_R is irrelevant for the kinetics and keep in L_R only those operators with zero mode. Then, the state $| F \rangle$ will look like $| \Psi \rangle$ with cluster function

$$\gamma(t) = w_0 t. \tag{34}$$

In fact, mode coupling affects the kinetics and leads to a coupled system of equations for $\gamma(t)$ and $\sigma_m(t)$.

Employing the general scheme of section 5, we are in a position to state the kinetics equation for $\gamma(t)$. On projecting both sides of (29) onto condensate $\langle m |$, it follows that

$$\Omega^{-1} \dot{\gamma} \langle m | Q_0 | \Psi \rangle = \langle m | \check{L} | \Psi \rangle. \tag{35}$$

From now on, we employ the pairing correlation model on a statistically homogeneous lattice, and so truncate S after

$$S = S_{aa} + S_{bb} + S_{ab}. \tag{36}$$

The evaluation of the necessary matrix elements is facilitated by the Baker–Campbell–Hausdorff formula for canonical transformation of creation and annihilation operators [37], and yields

$$\bar{a}_0 = a_o \qquad \overline{a_k^+} = a_k^+ \tag{37a}$$

$$\bar{a}_k = a_k + \sigma_{ab}(k, t)b_{-k}^{\pm}a_0 b_0 + 2\sigma_{aa}(k, t)a_{-k}^{\pm}a_0^2 \tag{37b}$$

$$\overline{a_0^+} = a_0^+ - \sum{}' \sigma_{ab}(k, t)a_k^+ b_{-k}^{\pm} b_0 - 2\sum{}' \sigma_{aa}(k, t)a_k^+ a_{-k}^{\pm}a_0. \tag{37c}$$

By symmetry, the canonical transformation with operators of B particles can be written. It is hoped that some points in the calculation of matrix element $M = \langle m|\bar{L}|\Psi\rangle$ will help one to use (37) in other cases. First, the expectaton value of M in (35) is given between condensate states $\langle m|$ and $|\Psi\rangle$. Employing (37) and identities $\langle C|a_k^+ = \langle C|b_k^+ = 0$ unless $k \neq 0$, where $\langle C|$ is arbitrary condensate state, M can be written in the form

$$M = \Omega^{-1}\langle m| \sum_k (w_k \bar{a}_k \bar{b}_{-k} - w_k a_0^+ b_0^+ \bar{a}_k \bar{b}_{-k})|\Psi\rangle.$$

Contributions to M from operators with $k = 0$ and $k \neq 0$ result in the final equation

$$\dot{\gamma}(t) = w_0 + \sum{}' w_k \sigma_{ab}(k, t). \tag{38}$$

If correlations are absent, as is expected in the case $\sigma_{ab} = 0$, then the cluster function $\gamma(t)$ is identical to (34). Eliminating $\dot{\gamma}(t)$ from (38) and (33), we obtain the rate equation for concentration $c_a(t) = \Omega^{-1}\langle n_a(t)\rangle$

$$\partial_t c_a(t) = -\mathrm{k}(t)c_a(t)c_b(t) \tag{39a}$$

where

$$\mathrm{k}(t) = w_0 + \sum{}' w_k \sigma_{bb}(k, t) = \dot{\gamma}(t). \tag{39b}$$

To improve (39b) still further, we can enlarge the basis set in operator S beyond the pairing model (36); this, however, leaves the relationship (39b) unchanged.

In this section we assume as self-evident that projection of (29) should be taken on vector $\langle m|$. In principle, one can find a projection on state $\langle z|$; *this entails the identity* $0 = 0$, *and gives no new information.*

7. Equations for pair correlation functions

We are thus led to consider equations for pair correlation functions $g_{ab}(q, t)$. To do this, we first project both sides of equation (29) onto vector $\langle z|Q_{aq}Q_{b-q} = \langle z|a_q b_{-q}$, getting

$$\langle z|a_0 b_0|\Psi\rangle t)\rangle\dot{\sigma}_{ab}(q, t) = \langle z|a_q b_{-q}\bar{L}|\Psi(t)\rangle. \tag{40}$$

In contrast to the calculations in section 6, here, the projection is carried out on vector $\langle z|$, involving full statistical averaging over configurations of particles and over particle numbers. On decomposing the Liouvillean L_R in RHS of (40) in the number of operators with zero mode (see appendix 1), calculations of matrix elements become easier to make. We restrict attention to a typical matrix element arising from operator $\bar{H}_3$ (see appendix 1), i.e. consider $M_3 = \langle z|a_q b_{-q} \bar{H}_3|\Psi(t)\rangle$, or

$$M_3 = \langle z|a_q b_{-q} \Omega^{-1} \sum_k{}' w_k \overline{a_0^+ b_0^+} \, \bar{a}_k \bar{b}_{-k}|\Psi(t)\rangle. \tag{41}$$

Making use of (37), the vector $\bar{a}_k \bar{b}_{-k}|\Psi(t)\rangle$ is seen to be a linear combination of pure condensate state together with three other states, each representing exactly one excited pair of particles either of type $a_k^+ a_{-k}^+$, $a_k^+ b_{-k}^+$, or $b_k^+ b_{-k}^+$, above the zero mode condensate. Subsequent operation by $a_0^+ b_0^+$ on these states gives a set of states in which pairs of particles either add to the excited states or add to the condensate. Thus, non-zero matrix elements of $\bar{H}_3$ between $|\Psi(t)\rangle$ and excited bra-state $\langle z|a_q b_{-q}$, emerge from the component of vector $\bar{a}_k \bar{b}_{-k}|\Psi(t)\rangle$ containing precisely a single pair $a_k^+ b_{-k}^+$ above the condensate. We get

$$M_3 = \frac{w_q}{\Omega}(\sigma_{ab}^2(q,t) + 4\sigma_{aa}(q,t)\sigma_{bb}(q,t))\langle z|a_0^2 b_0^2|\Psi(t)\rangle$$

$$- \sigma_{ab}(q,t)\sum_k{}'\frac{w_k}{\Omega}\sigma_{ab}(k,t)\langle z|(a_0^+ a_0 + b_0 b_0^+)a_0 b_0|\Psi(t)\rangle. \tag{42}$$

The first line of (42) exactly coincides with matrix element $\langle z|a_q b_{-q}L_R'|\Psi(t)\rangle$. Hence, these terms cancel each other in the full matrix element (40). The origin of the cancellation of the nonlinear $\sigma_{\lambda\lambda'}$ terms is in the balance structure of operator L_R involving the gain and loss terms. This peculiarity in the rate equation permits us to find in section 9 an analytical solution for σ_{ab} as a function of the concentrations $c_\lambda(t)$.

By performing straightforward manipulations with Bose algebra for other matrix elements M_i and implementing the thermodynamic limit

$$\langle z|a_0^\alpha b_0^\beta|\Psi(t)\rangle = \langle n_a(t)\rangle^\alpha \langle n_b(t)\rangle^\beta \tag{43}$$

$(\alpha, \beta = 1, 2$ and $\langle n_\lambda(t)\rangle \gg 1$, $\Omega \gg 1$, $\lambda = a, b)$ in the kinetics equation (40) with cluster functions $\sigma_{\lambda\lambda'}(q,t)$ defined by

$$\sigma_{ab}(q,t) = \Omega^{-1}g_{ab}(q,t)$$
$$2\sigma_{\lambda\lambda}(q,t) = \Omega^{-1}g_{\lambda\lambda}(q,t) \tag{44}$$

we arrive at a net kinetics equation for $g_{ab}(q,t)$ as follows:

$$\dot{g}_{ab}(q,t) = -(D_{aq} + D_{bq})q\,_{ab}(q,t) - w_q - T_q(t) + c(t)g_{ab}(q,t)T_0(t) - w_q c_a(t)g_{aa}(q,t)$$
$$- w_q c_b(t)g_{bb}(q,t). \tag{45}$$

Here, $c(t) = c_a(t) + c_b(t)$ is total concentration, and shorthand notation is used for

$$T_q(t) = \Omega^{-1}\sum_k{}' w_k g_{ab}(q-k,t). \tag{46}$$

It is useful to rewrite the expression for $k(t)$, (39b), in the form

$$k(t) = w_0 + T_0(t). \tag{47}$$

In order for the description to be self-contained, we should derive kinetics equations for $g_{bb}(q, t)$ and $g_{aa}(q, t)$ by projecting (29) onto $\langle z | Q_{\lambda q} Q_{\lambda -q}$, followed by passage to the thermodynamic limit (43). For A particles, the following equation holds true

$$\dot{g}_{aa}(q, t) = -2D_{aq}g_{aa}(q, t) + 2k(t)c_b(t)g_{aa}(q, t) - \tfrac{1}{2}w_q c_b(t)g_{ab}(q, t). \qquad (48)$$

The equation for $g_{bb}(q, t)$ is analogous to $g_{aa}(q, t)$ and requires only change of indices $a \rightleftarrows b$.

We have reached one of the central results of this paper: equations (45–48) for the pair correlation functions supplemented by (39a) formulate the pairing correlation model of DLR.

8. Two-body approximation: the Smoluchowski kinetics

Thus far in the paper, we have been able to proceed without having to use any explicit form and sense of the correlation functions. Pursuing the logic of the subject, we discuss general properties of the $g_{\lambda\lambda'}$ at low concentration and strong coupling limit. At low concentrations, $c_\lambda \rightarrow 0$, a leading contribution to (45) is provided by the first three terms of the RHS, and (45) becomes linear in g_{ab} and closed:

$$\dot{g}_{ab}(q, t) = -(D_{aq} + D_{bq})g_{ab}(q, t) - w_q - T_q(t). \qquad (49)$$

As for the general properties of the state vector $|F(t)\rangle$ in this approximation, it can be regarded as created by a singly excited pair of A–B above the condensate. The many-body character of recombination is missing here. By drawing an analogy with quantum methods, we can consider the Smoluchowski approximation (49) as resulting from the Tamm–Dancoff approximation [22] or, in the language of perturbation theory, from summation of ladder diagrams.

To show that g_{ab} leads to the Smoluchowski result for the effective rate of recombination, let us specify the elementary rate of pair recombination

$$w_q = 2D \sum_{i=1}^{3} \cos(q_i) \qquad (50a)$$

where D is the mutual diffusion rate, $D = D_a + D_b$. The form (50a) is responsible for infinitely fast local recombination of pairs of particles. A finite rate (50a) is derived through renormalization [38] of the Liouvillean of the fast recombination to an effective one, L_R (10), with diffusion controlling and non-local (in coordinate representation) rate

$$w(r) = D\delta(|r| - 1) = D \sum_{\alpha=1}^{6} \delta(r - e_\alpha) \qquad (50b)$$

with e_α being primitive vectors of the simple cubic lattice. The renormalized form of L_R is preferable for our further analysis in section 9, as it does not lead to the ambiguity that would arise from the remaining terms in (45) in the limit $w_q \rightarrow \infty$, $c_\lambda \rightarrow 0$ if the non-renormalized version of L_R was chosen. Fast recombination implies

also that no cell of the lattice contains particles of more than one kind. Thus, we subject the pair correlation function $g_{ab}(r, t)$ to condition

$$g_{ab}(r=0, t) = 0. \tag{51}$$

By Fourier inversion of (49) and (46), one finds

$$\dot{g}_{ab}(r, t) = \sum_{\alpha=1}^{6} D(r, r+e_\alpha)(g_{ab}(r+e_\alpha, t) - g_{ab}(r, t)) - B(r, t) \tag{52}$$

where $B(r, t) = w(r)(1 + g_{ab}(r, t))$. Here, the lattice Laplacian is written in a more general form that accounts for the diffusion on the non-uniform lattice. Validity of (52) follows from derivation of (45–48) which holds true for the arbitrary inhomogeneous function $D(r, r+e)$.

To keep zero value for the function $g_{ab}(r=0, t)$ in time, we impose the following condition [10] on diffusion rates

$$D(0, e_\alpha) = 0 \qquad \text{where } \alpha = 1, \ldots, 6. \tag{53}$$

This equation is consistent with the diffusion part of the effective Liouvillean found in [38]. Equation (51) is satisfied on the lattice at any time, if (51) is satisfied at $t = 0$. The proof is clear. At $r = 0$, we have $w(0) = 0$, $B(0, t) = 0$ and (52) becomes $\dot{g}_{ab}(0, t) = 0$, so, $g_{ab}(0, t) = 0$ if $g_{ab}(0, 0) = 0$. Equations (51) and (53) serve as the 'boundary' conditions to (52). Another way of viewing the non-intersection of configurations of A and B particles is to consider the 'jumping' of a particle, say A, with rate D towards a particle B, fixed at cell $r = 0$. By (53), the lattice on which the diffusion of A happens has six broken bonds with a common cell at $r = 0$. From this point of view, the A particle cannot appear at $r = 0$ together with the B particle. Due to non-local recombination (50b), the broken bonds $(0-e_\alpha)$ do not affect recombination when the particles are placed in the adjacent cells, but the broken bonds prevent the particles from making contact.

In seeking a solution to (52), we invoke the Green function (GF) technique [39]. The GF $\tilde{\mathscr{G}}^0(r, x)$ for a uniform lattice is ruled by

$$\varepsilon \tilde{\mathscr{G}}^0(r, x) = D \sum_{\alpha=1}^{6} (\tilde{\mathscr{G}}^0(r+e_\alpha, x) - \tilde{\mathscr{G}}^0(r, x)) + \delta(r-x). \tag{54}$$

The tilde ($\sim$) signifies the Laplace image function with variable ε conjugated to time t. The diffusion rate over the arbitrary bond $(r, r+e)$ reads

$$D(r, r+e) = D + \xi(r, r+e), \tag{55}$$

where $\xi(r, r+e)$ is the localized perturbation on the uniform lattice, so that $\xi(r, r+e) = -D$, if bond $(r, r+e)$ belongs to the central cell $r = 0$, and $\xi(r, r+e) = 0$ otherwise. Then, (52) is equivalent to

$$\tilde{g}_{ab}(r) = \sum_{x} \tilde{\mathscr{G}}^0(r, x)\left(\sum_{\alpha=1}^{6} \xi(x, x+e_\alpha)(\tilde{g}_{ab}(x+e_\alpha) - \tilde{g}_{ab}(x)) - \bar{B}(x)\right)$$

where $\bar{B}(x) = w(x)(\varepsilon^{-1} + \tilde{g}_{ab}(x))$. The sum over x in this equation is restricted to cell $x = 0$ and six neighbouring cells $x = e_\alpha$, $\alpha = 1, \ldots, 6$, since both function $w(x)$, (50b),

and $\xi(x, x + e_a)$ are localized in space. Taken in conjunction with $\tilde{g}_{ab}(x=0)=0$, it is a simple exercise to find the solution for the correlation function

$$\tilde{g}_{ab}(r) = -\varepsilon^{-1} D \sum_{a=1}^{\sigma} \tilde{\mathcal{G}}(r, e_a) + \sum_x \tilde{\mathcal{G}}(r, x) g_{ab}(x, t=0) \tag{56a}$$

where combination

$$\tilde{\mathcal{G}}(r, x) = \tilde{\mathcal{G}}^0(r, x) - \frac{\tilde{\mathcal{G}}^0(r, 0)\tilde{\mathcal{G}}^0(0, x)}{\tilde{\mathcal{G}}^0(0, 0)}, \tag{56b}$$

stands for GF for diffusion from cell x to r on an uniform lattice containing an infinitely absorbing trap at $r=0$ [40].

The solutions (56) for g_{ab} permits us to find an effective rate of recombination $k(t)$. With the aid of (46), (47 and (50b), we have a general expression

$$k(t) = 6D + D \sum_{a=1}^{6} g_{ab}(e_a, t). \tag{57}$$

Inserting (56) into (57), we arrive at the final result

$$\tilde{k}(\varepsilon) = \tilde{k}^0(\varepsilon) + \sum_x \frac{\tilde{\mathcal{G}}^0(0, x)}{\tilde{\mathcal{G}}^0(0, 0)} g_{ab}(x, t=0) \tag{58a}$$

with

$$\tilde{k}^0(\varepsilon) = 6D\varepsilon^{-1} + \tilde{T}_0 = (\varepsilon \tilde{\mathcal{G}}^0(0, 0))^{-1} - 1. \tag{58b}$$

The later formula demonstrates the well known result for recombination rate when correlations between $A-B$ pairs are absent. In deriving (58), use has been made of the properties of GF for a uniform lattice (see appendix 2). Asymptotic behaviour (58) at $t \to \infty$ ($\varepsilon \to 0$), yields $k(t) = k^0(t) = 6D/I_w$, where $I_w \approx 1.51$ is the Watson integral [40]. In the continuum limit, i.e. $r \gg 1$ and $t \to \infty$, correlation function $g_{ab}(r, t)$ is determined by the GF

$$\tilde{\mathcal{G}}^0(r, \varepsilon) = (4\pi Dr)^{-1} \exp\left(-r\sqrt{\varepsilon/D}\right) \tag{59}$$

and obeys

$$g_{ab}(r, t) \to -1/(4\pi r) \tag{60}$$

which is merely the solution of the Laplace equation $\Delta g_{ab}(r, t) = 0$.

The long-range character of g_{ab} suggests inclusion in the discussion of many-body effects.

9. Role of pairing correlations

9.1. Exclusion principle

Having got the solution of the two-body problem, we are going to analyse the full system (45–48). The state vector $|F\rangle$ in this case is represented by a mixture of pairing correlations created from the condensate with operators $(Q_{\lambda k}^+ Q_{\lambda-k}^+)^m$, $m \geq 2$. The state of the same type is known, and referred to as the random phase approximation.

Before studying the question of how pairing correlations affect the effective rate of recombination, we first prove that (45–48) provides non-intersection of the configurations of particles, i.e. $g_{ab}(r, t)$ satisfies (51). In the two-body problem, the constraint (51) has been guaranteed by 'deformation' of the lattice, i.e. with property (53). For the condition $g_{ab}(r=0, t)=0$ to be valid now, it is tempting to keep the topological restriction (53) in the rate equations for correlation functions $g_{aa}(r=0, t)$ and $g_{bb}(r=0, t)$. In other words, we want to forbid the two particles of one kind occurring in any cell, i.e. when the relative distance between particles of one kind equals zero. From a statistical point of view, these particles should obey the Pauli statistics. Actually, it is the Pauli statistics which led us to the Liouvillean (10) with renormalized (diffusion-limited) rate (50) [38]. The fact that in deriving (45–48), we ignored the Pauli statistics and have made algebraic manipulations in the framework of the Bose statistics, can now be remedied by imposing the additional restrictions

$$g_{\lambda\lambda}(r=0, t)=0 \tag{61}$$

where $\lambda = a, b$. These conditions are satisfied on the 'deformed' lattice. Indeed, (50a) is the same as $w_q = 6D - (D_{aq} + D_{bq})$, so, we reformulate (45) in coordinate representation

$$\dot{g}_{ab}(r, t) = D\Delta g_{ab}(r, t) - B(r, t) + c(t)g_{ab}(r, t)T_0(t) - J(r, t) \tag{62a}$$

with definition

$$J(r, t) = D \sum_{\lambda=a, b} c_\lambda(t)(6 + \Delta)g_{\lambda\lambda}(r, t). \tag{62b}$$

Laplacian $D\Delta$ on the 'deformed' lattice acts as

$$\nabla D \nabla g_{\lambda\lambda}(r, t) \equiv \sum_{\alpha=1}^{6} D(r, r+e_\alpha)(g_{\lambda\lambda}(r+e_\alpha, t) - g_{\lambda\lambda}(r, t)).$$

From (53), it follows straightforwardly that $\nabla D \nabla g_{\lambda\lambda}(0, t) = 0$. Thus, the non-local part of (62) gives no contribution at any instant of time to the equation for $\dot{g}_{ab}(r=0, t)$. The same is true for the kinetics equations for $g_{\lambda\lambda}(r=0, t)$ derived from (48) by Fourier transformation to coordinate space. On noting $B(r=0, t)=0$, we obtain a homogeneous and closed system of kinetics equations for $g_{\lambda'\lambda}(r=0, t)$. This conclusion validates the exclusion principle for any kind of particle, i.e. (51) and (61), if it takes place at $t=0$.

9.2. Screening of g_{ab} in monomolecular DLR

The simplest case for exploring the full system (45–48) is that of monomolecular kinetics when one component, say B, is in excess. Then, the full concentration $c(t)$ is practically constant over time, i.e. $c(t) \approx c_b$. The asymptotic behaviour of the effective reaction rate at the low concentration limit is expected to be governed by k^0, so $T_0(t) \rightarrow -6D(I_w - 1)/I_w$ at $t \rightarrow \infty$. The sign of $T_0(t)$ is of particular value. Generally speaking, an exact value of $T_0(t)$, along with the value of the first approximation of

$T_0(t)$, is also negative since $g_{ab}(r, t) < 0$, for $r \geqslant 1$. So, it is helpful to define a positive variable κ^2 by putting

$$D\kappa^2 = -cT_0 \tag{63}$$

then (62) results in

$$\dot{g}_{ab}(r, t) = (\nabla D\nabla - D\kappa^2)g_{ab}(r, t) - B(r, t) - J(r, t). \tag{64}$$

To find a solution to (64), let us neglect pairings A–A and B–B, so dropping the function $J(r, t)$ from (64). Then (64) becomes a closed self-consistent equation. Considerable reduction in the mathematics of the problem occurs in the low concentration limit when κ^2 is practically constant, $\kappa^2 = 6c(I_w - 1)/I_w$. By comparing (64) and (52), one obtains a solution $\tilde{g}_{ab}(r, \varepsilon)$ in the same form as (56a), but argument ε in the GF $\mathscr{G}(r, x; \varepsilon)$ should now be replaced by variable $\varepsilon' = \varepsilon + D\kappa^2$, i.e.

$$\tilde{g}_{ab}(r, \varepsilon = -\varepsilon^{-1}D\sum_{a=1}^{6} \mathscr{G}(r, e_a; \varepsilon') + \sum_x \mathscr{G}(r, x; \varepsilon')g_{ab}(x, t=0, \tag{65}$$

where we have explicitly shown the dependence of $\mathscr{G}$ on ε. Making use of (59) at $\varepsilon \to 0$ or $\varepsilon' \to D\kappa^2$, we infer

$$g_{ab}(r, t) \to -r^{-1}\exp{(-r\kappa)} \qquad \text{at } t \to \infty. \tag{66}$$

The occurrence of screening in $g_{ab}(r, t)$ can be readily seen from (64) by rewriting the equation in the Laplace–Fourier domain. Then, the function $\tilde{g}_{ab}(q, \varepsilon)$ will have a pole at frequency $\varepsilon = D(q^2 + \kappa^2)$. The shift from diffusion mode reveals the collective mode.

The physics behind the screening, or in other words the exponential suppression of the correlations into pairs A–B, is clear. Expression (66) tell us that when a particle, say A, jumps from cell r towards a particle B fixed at cell 0, the A particle can recombine both with the B particles placed around cell 0 and with the B at 0.

The screening gives rise to a change of the rate constant k, (58). To bring this effect into the formalism, we use the above-mentioned property that the solution $\tilde{g}_{ab}(r, \varepsilon')$ coincides in form with the two-body $\tilde{g}_{ab}(r, \varepsilon)$. So, disregarding the initial correlations in (58b), the many-body rate constant takes the form

$$\tilde{k}(\varepsilon) = (\varepsilon\mathscr{G}^0(0, 0; \varepsilon + D\kappa^2))^{-1} - 1. \tag{67}$$

Consider the limit $c_b \ll 1$. The GF $\mathscr{G}^0(0, 0; \varepsilon')$ on the uniform lattice depends on ε' as $\sqrt{\varepsilon'}$ at small ε'. More precisely, $\mathscr{G}^0(0, 0; \varepsilon') = I_w/6D - (4\pi D)^{-1}\sqrt{\varepsilon'/D}$ at $\varepsilon' \to 0$ [41]. On inserting this result into (67) and putting $\varepsilon \to 0$ ($t \to \infty$), $c_b \ll 1$, we get

$$k(\infty) = k^0(\infty)\left(1 + \frac{3\kappa}{2\pi I_w}\right). \tag{68}$$

From (68) and (63), the correction to the Smoluchowski rate constant is proportional to $\sqrt{c_b}$ at $c_b \ll 1$. The square root dependence on c_b of $k(\infty)$ has been found in another way in [42, 43]. The consistency of both methods is not surprising since the summed most divergent terms, $\approx (q^{-2})^n$, in perturbation theory are proved [43] to be the same as in the Debye–Huckel theory (DH), which is equivalent to a random phase approximation accounting for multiple pair excitations $(Q_{aq}^+Q_{a-q}^+)^n$. We can strengthen the formal analogy with DH theory by noting that the inverse screening (pairing) length has just the same concentration dependence as the inverse Debye length for a system of ions, i.e. $\kappa \approx \sqrt{c_b}$.

The result (68) can be directly applied to DLR with comparable concentrations of particles. For this case, the full concentation, $c(t)$, tends to a constant value $c(t) \rightarrow$ $|c_a(0) - c_b(0)| \neq 0$ at $t \rightarrow \infty$, so $\kappa(t) \rightarrow$ constant, hence, the solution for k, (67) applies.

9.3. Slowing kinetics for the bimolecular DLR

Our particular interest is in DLR for equal concentrations of the species, i.e. $c_a(t) = c_b(t)$. Nonlinearity of the system (45–48) rules out an exact analytical solution, forcing one to use approximations. For the sake of simplicity, we begin with kinetics without pairing of A–A and B–B, i.e. put $S_{aa} = 0$, $S_{bb} = 0$, and thus discard $J(r, t)$ in (62). Introduce the auxiliary function

$$h(r, t) = g_{ab}(r, t)\zeta_1(t) \qquad \text{where } \zeta_1(t) = \exp\left(2\int_0^t \varphi(\tau)\, d\tau\right) \qquad (69)$$

and $\varphi(t) = -c_a(t)T_0(t)$. From (62) and (69), we immediately obtain the equation for $h(r, t)$

$$\dot{h}(r, t) = \nabla D \nabla h(r, t) - w(r)(\zeta_1(t) + h(r, t)). \qquad (70)$$

Repeatedly invoking the method of solution (52) presented in section 8, we obtain

$$\tilde{h}(r) = -D\xi_1 \sum_{\alpha=1}^{6} \mathcal{G}(r, e_\alpha) + \sum_x \mathcal{G}(r, x) g_{ab}(x, t=0). \qquad (71)$$

On Laplace inverting (71) and turning back to $g_{ab}(r, t)$, we arrive at the final result for the correlaton function

$$g_{ab}(r, t) = \zeta_1^{-1}(t)\left(-D\int_0^t \zeta_1(\tau) \sum_{\alpha=1}^{6} \mathcal{G}(r, e_\alpha; t-\tau)\, d\tau + \sum_x \mathcal{G}(r, x; t) g_{ab}(x, t=0)\right) \qquad (72)$$

Function $\zeta_1(t)$ can be rewritten in tems of the concentration $c_a(t)$. In so doing, we eliminate $T_0(t)$ from $\varphi(t)$ by refering to (47) and (39) and writing $\varphi(t) = \partial_t \ln(c_a(t)) + 6Dc_a(t)$. Combining this with (69), we get

$$\zeta_1(t) = \left(\frac{c_a(t)}{c_a(0)}\right)^2 \zeta_2(t) \qquad \zeta_2(t) = \exp\left(12D\int_0^t c_a(\tau)\, d\tau\right). \qquad (73)$$

Part of the answer for $k(\infty)$ comes from the first term in the RHS of (72) at $t \rightarrow \infty$ ($\varepsilon \rightarrow 0$), namely

$$-D\sum_{\alpha=1}^{6} \tilde{\mathcal{G}}(r, e_\alpha, \varepsilon=0).$$

Its contribution to the effective rate of recombination (57) yields the Smoluchowski rate constant (see appendix 2)

$$k^0(\infty) = 6D - D\sum_{\alpha=1}^{6} \tilde{\mathcal{G}}^0(0, e_\alpha; \varepsilon=0)/\tilde{\mathcal{G}}^0(0, 0; \varepsilon=0) = 6D/l_w. \qquad (74)$$

Examine now the role played by the residual term in (72) resulting from the initial

conditions, $g_{ab}(x, t=0)$. Due to (73), this term is proportional to $c_a^{-2}(t)$, thus, its contribution becomes predominant at $c_a \to 0$. Moreover, it breaks down the second-power dependence on concentration in the material balance equation, giving the final equation

$$\dot{c}_a = -\mathcal{k}^0 c_a^2 + Dc_a^2(0)\zeta_2^{-1}(t)Gt^{-3/2}. \tag{75}$$

Here, the factor $t^{-3/2}$ comes from the diffusional asymptotic of $\mathcal{G}(e_a, x; t)$, and the positive constant G ($\approx D^{-3/2}$) follows from summation over x and e_a. This equation exhibits a slowing of the kinetics. Indeed, assuming $c_a(t) \approx t^{-3/4}$, the LHS of (75) is found to fall to zero faster than the separate terms of the RHS, so as expected

$$c_a(t) = (Dc_a^2(0)\zeta_2^{-1}(t)(G/\mathcal{k}^0)t^{-3/2})^{1/2} \approx (t/D)^{-3/4} \tag{76}$$

at some intermediate time interval at which $\zeta_2^{-1}(t) \approx 1$. This dependence can certainly be ascribed to collective correlations of particles. However, as we go to $t \to \infty$, then $\zeta_2^{-1}(t) \to 0$, so the law $\approx t^{-3/4}$ falls off, and $c_a(t)$ undergoes transition to the law $c_a(t) \approx t^{-1}$.

For the purposes of discrimination between $t^{-3/4}$ and t^{-1} kinetics, one can take criterion

$$D \int_0^{t^*} c_a(\tau)\, d\tau \approx 1$$

setting a characteristic time scale

$$t^* \approx D^{-1}c_a^{-4}(0) \tag{77}$$

within which the kinetics differ from the familiar action mass law. After the time t^*, the pairings $A-B$ are destroyed or 'burned' due to diffusional spreading of the reagents. In passing to dimensional units, D^{-1} in the above estimate (77) should be replaced by $l^2 D^{-1}$, where l is the lattice constant and $c_a(0)$ is the density number.

It remains to check on the validity of the stated assertion that on the intermediate asymptotic, the law $c_a(t) \approx t^{-3/4}$ does not affect $A-A$ and $B-B$ pairings. Simple inspection shows that (48), on transforming to coordinate space, has the solution

$$g_{aa}(r, t) = \left(\frac{c_a(0)}{c_a(t)}\right)^2 \left\{ \sum_x P_a(x \to r; t)g_{aa}(x, 0) \right.$$

$$\left. -\frac{1}{2}\int_0^t d\tau c_b(\tau)\left(\frac{c_a(\tau)}{c_a(0)}\right)^2 \sum_x P_a(x \to r; t-\tau)w(x)g_{ab}(x, \tau)\right\} \tag{78}$$

where $P_a(x \to r; t)$ is the GF for transition of A particle on the 'deformed' lattice, with $P_a(x \to 0; t) = 0$ and $P_a(x \to 0; t) \neq \mathcal{G}(x, 0; t)$ holding. Substitution of (78) into (62) gives additional terms in the g_{ab} which are singular of the type $c^{-1}(t)$, i.e. they have smaller singularity than $c^{-2}(t)$ as $c \to 0$. The corresponding contribution to the action mass law falls faster than $t^{-3/4}$ and can be dropped. So, the pairings $A-A$ and $B-B$, as has been assumed, are immaterial at the asymptotic.

Numerical calculations are necessary to derive more details about the physical meaning of (45–48).

One remark is noteworthy before concluding. Equations like (75), but without the exponential factor ζ_2, have been derived in a different fashion in [12, 14].

10. Summary and outlook

Correlation effects between particles in DLR are known to have been investigated by various approaches; each of these needs an approximation scheme to reduce the number of degrees of freedom. These approaches can be cast into four classes: (1) path integral formalism based on functional formulation of (9) [44, 45]; (2) diagrammatic Green function perturbation methods [13]; (3) approaches using the model Liouvillean [14]; (4) truncated hierarchy of a rate equations [9–12, 15, 46]. The time–dependent CCA developed in this paper belongs to the fourth method. It seems to have the advantage of being simpler than the alternative methods of calculation of collective and correlation effects relying on the mean field approximations†.

For the scenario of DLR described by the Liouvillean (10), we have derived governing kinetics equations (45–48) for pair correlation functions which *completely* incorporate pairing correlations in the many-body system, leaving higher-order correlations out of the discussion. The Fock space associated with the kinetics encompasses pairing excitations carrying a vanishing total wavevector. In the original CCA this approximation is referred to as the SUB2 approximation (or coupled pair approximation), and is assumed to make a leading contribution to the correlation properties of the system in hand [26, 27]. We believe SUB2 captures the major fraction of correlations to the rate equation (75), leaving only a minor part for SUBn, $n \geqslant 3$. Although, in principle, any type of SUBn can be introduced in the systematic mathematical treatment, in practice, only SUB2 gives a closed theory, the SUB1 terms involving single–particle excitations, i.e. (16a), are dropped due to statistical homogeneity.

We have called the SUB2 approach a pairing correlation approximation. It carries an obvious sense of the division of the system into pairs of particles with total wavevector 0, and quite distinct from formation of the chemical bonding. A minimal basis space relevant for this purpose is spanned by the states of the type $(Q_{\vec{k}}^{+} Q_{\vec{r}-k}^{+})^n |C\rangle$, where $|C\rangle$ is a condensate. Having restricted the many-body basis, the correlation problem was formulated as a solution to (45–48) for correlation functions $g_{\lambda\lambda'}(r, t)$ which are derived by projecting kinetics equations for $|F(t)\rangle$ onto a given basis set. Physically, this projection means averaging over configurations and particle numbers.

To prepare the ground for the general case, we have solved (45–48) in the two-body approximation when $c_\lambda(t) \to 0$ and the system is reduced to a single equation (49). In the strong coupling limit, the elementary rate of pair recombination is nonlocal in space and diffusion-limited, equation (50b). The exact solution for $g_{ab}(r, t)$ reproduces the Smoluchowski result with the rate (58b). The solution of the two-body approximation is important for two reasons.

First, rapidly recombining particles give rise to the necessity to sum, in diagrammatic language, the latter diagrams in order to renormalize the elementary rate $w(r)$, equation (50), to the effective two-body rate $\kappa(t)$, equation (58). We have referred to this calculation as the strong-coupling limit. In this way, we have obtained the long-range correlation function $g_{ab}(r, t) \to r^{-1}$, at $r \to \infty$, $t \to \infty$. So, we have been faced

with the second problem of how to incorporate the collective properties emerging from long-distance effects. The way to do this is in using an RPA-inspired approach. There are two distinctive features of the CCA, namely, incorporating into the analysis both short-range and long-range physics (by accounting for ladder and ring diagrams along with the so-called 'condensate potential' terms) without performing perturbation calculations; this enables successful application of the CCA for exploring collective and correlation effects in DLR.

In section 9.2, we have solved (45–48) for a monomolecular regime neglecting A–A and B–B pairings. The corresponding solution $\tilde{g}_{ab}(r, \varepsilon)$ coincides in form with the two-body $\tilde{g}_{ab}(r, \varepsilon)$, but all GF in the latter have argument $\varepsilon + D\kappa^2$ instead of ε. This leads to an exponential screening of $\tilde{g}_{ab}(r, \varepsilon)$; also asymptotic behaviour of k reproduces the result [42, 43] at $c_b \ll 1$. Within the same general framework, we have treated bimolecular recombination, i.e. the case $c_a(t) = c_b(t)$, where, due to the initial value problem of DLR, pre-asymptotic kinetics have been found to be $c_a(t) \approx t^{-3/4}$, however, $c_a(t) \approx t^{-1}$ at true asymptotic at $t \to \infty$.

Generally, the pairing model can be explored from the viewpoint of approximations of the L_R, not in the vector state $|F\rangle$. Indeed, we can reduce the whole L_R by retaining only pairing interactions by expansion of L_R in number of operators with zero mode, and then seeing if anything useful emerges. This point of view was adopted in [14]. The authors found $c_a(t) \approx t^{-3/4}$ at $t \to \infty$. This result conflicts with our one, as we have found $c_a(t) \approx t^{-1}$ at $t \to \infty$. Note that pairing the Liouvillean L_R does not contain term H_{12} (see appendix 1) accounting for ladder diagrams, and so possesses no means of treating accurately the strong coupling limit. We leave the detailed comparison of the two formalisms to the reader.

The simplicity of the CCA approach for DLR can promote further thinking on this subject. If in this way, one gives up the idea of selecting an unorthodox basis set $\{Q_m^+\}$ which provides a large–scale separation of the phases in the volume, the present (SUB2) level of the description, nonetheless, offers ample opportunity for application of the CCA to the wide area of non-equilibrium classical systems. Our intention here is to list a few examples. Among them is exploring collective properties in systems showing Turing instability ('unstable condensate' in our language) [47]. We can speculate whether the screening length κ^{-1} tends to infinity if the concentration tends to a critical point. The practical essence of the foregoing discussion for the two-component systems remains the same for multicomponent systems. Explicit in the methodology is the use of the coupled cluster ansatz (27) with $S(t)$ in the SUB2 form

$$S(t) = \Omega^{-1} \sum_{\lambda, \lambda'} \sum_{k \neq 0} g_{\lambda\lambda'}(k, t) Q_{\lambda k}^+ Q_{\lambda'-k}^+$$

subscripts λ, λ' denoting species. Next, we project the master equation for $|F(t)\rangle$ governed by the relevant Liouvillean onto the pairing basis set, to obtain kinetics equations for $g_{\lambda\lambda'}(k, t)$. Finally, the third step involves solution of the kinetics equation as in sections 8 and 9. This work can be regarded as an extension of RPA to complex chemical kinetics. The aforementioned $S(t)$ is hinted at by the cluster operator S in the description of a Bose liquid [20]. It is remarkable that this form of S holds for a kinetical problem with non-Hermitian governing operator L.

Study of of cellular classical hydrodynamic systems [48] can be performed by the

CCA. Investigation of quantum hydrodynamics in the framework of the CCA has been done in [33].

Association and dissociation of charged reactants maybe causes no principle difficulties. Here, the Coulomb interactions favour the using of the pairing correlation approach.

The peculiarity of the kinetics of the $g_{ab}(r, t)$, that initial value conditions have a pronounced influence on the kinetics at time interval $D^{-1} < t < t^*$, gives rise to the question of how the pairing correlation model manifests itself in the scattering function [49] on that time interval.

From a qualitative retrospective, the exponential ansatz of the CCA is similar to putting by hand the exponential form of the density matrix in the formalism of the non-equilibrium statistical opertor (NESO) [50]. The NESO treatment was found to be useful for some cases [51]. However, the explicit forms of the exponents in NESO and CCA are quite different. Our objective in this paper was to illustrate the coupled cluster method for dealing with collective and correlation effects in DLR. It is too soon to discuss the applications of the method, though it is clear that it would call for a different appoach for analysis of correlations in classical many-body systems.

In the construction of the kinetics equations, the question of the applicability limits of the CCA naturally arises. This has been a salient problem of physical concern in this paper. As noted earlier [19, 20] the problem of extracting the limitations of the SUB2 should be recognized, and the usefulness of the theory is justified *a posteriorily*. The motivations for neglecting SUBn, $n \geqslant 3$, on formal grounds is a difficult task, just as using small parameter, $c(t)$, is not convincing.

Concluding, the main message conveyed in [19–21] is that the CCA is a universal language for the analysis of correlation effects in quantum systems. We can strengthen this opinion, applying the same words to far-from-equilibrium classical systems. The second quantization formalism for classical systems [25] supplimented with the CCA permits us to come back to the old problem of the classical cluster expansion [18] with the quantum mechanical language. Moreover, the coupled cluster appoach, it is felt, can bridge the language gap between classical and quantum methods in many-body systems. The reason for this is a similarity of presentation and exploring of the classical state vector $|F\rangle$ and its quantum counterpart [52].

Appendix 1

Decompose Liouvillean L_R into two parts, $L_R = L'_R - L''_R$, corresponding to the gain and the loss terms in (9). Then, expand L'_R and L''_R in the number of operators with zero mode by setting, for instance, for particles of A sort $a_k = \delta(k)a_0 + (1 - \delta(k))a_k$. It appears that L'_R will be represented with two different terms

$$L'_R = \Omega^{-1} w_0 a_0 b_0 + \Omega^{-1} {\sum_k}' w_k a_k b_{-k} \tag{A1}$$

and L''_R will contain the 12 following terms

$$L''_R = \Omega^{-1} \sum_q w_q \sum_{kk'} a^+_{k+q} b^+_{k'-q} a_k b_{k'} = \sum_{j=1}^{12} H_j \tag{A2}$$

.

where

$$H_1 = \Omega^{-1} w_0 a_0^+ b_0^+ a_0 b_0 \qquad\qquad H_2 = \Omega^{-1} \sum{}' w_0 a_0^+ b_k^+ a_0 b_k$$

$$H_3 = \Omega^{-1} \sum{}' w_k a_0^+ b_0^+ a_k b_{-k} \qquad\qquad H_4 = \Omega^{-1} \sum{}' w_k a_0^+ b_k^+ a_k b_0$$

$$H_5 = \Omega^{-1} \sum{}' w_k a_0^+ b_{q+k}^+ a_k b_q \qquad\qquad H_6 = \Omega^{-1} \sum{}' w_k a_k^+ b_{-k}^{\pm} a_0 b_0$$

$$H_7 = \Omega^{-1} \sum{}' w_k a_k^+ b_0^+ a_0 b_k \qquad\qquad H_8 = \Omega^{-1} \sum{}' w_k a_k^+ b_q^+ a_0 b_{k+q}$$

$$H_9 = \Omega^{-1} \sum{}' w_k a_{q+k}^+ b_0^+ a_q b_k \qquad\qquad H_{10} = \Omega^{-1} \sum{}' w_0 a_k^+ b_0^+ a_k b_0$$

$$H_{11} = \Omega^{-1} \sum{}' w_k a_q^+ b_k^+ a_{k+q} b_0 \qquad\qquad H_{12} = \Omega^{-1} \sum{}' w_q a_{k+q}^+ b_{k'-q}^+ a_k b_{k'}.$$

All primed sums are over non-zero modes.

Calculation of the matrix elements $M_j = \langle z | a_k b_{-k} \bar{H}_j | \Psi(t) \rangle$ is straightforward, yet of little practical value. The net result to (45) from three operators H_1, H_2 and H_{10} is of order Ω^{-1}, thus they cannot bring any contribution to the RHS of (45). Each of the matrix elements M_5, M_8, M_9, M_{11} vanishes. The M_6 and M_{12} contribute to the second and third term of the RHS of (45). Finally, elements M_3, M_4, M_7 are also sizable.

Appendix 2

Equation (54) for the GF on a uniform lattice yields three profitable realtionships. On putting in (54) $r = 0$, $x = 0$, we find the first relationship

$$\varepsilon \mathcal{G}^0(1, 0) - 1 = 6D(\mathcal{G}^0(1, 0) - \mathcal{G}^0(0, 0)) \tag{B.1}$$

where $\mathcal{G}^0(1, 0) \equiv \mathcal{G}^0(e_\alpha, 0)$ for arbitrary $\alpha = 1, \ldots, 6$. The next relationship follows from (54) for $r = 0$ and arbitrary $x \neq 0$:

$$(\varepsilon + 6D)\,\mathcal{G}^0(0, x) = D \sum_{\alpha=1}^{6} \mathcal{G}^0(e_\alpha, x). \tag{B2}$$

Finally, relying on (B1), (B2) and definition $\mathcal{G}(r, x)$, (56b), we have

$$\bar{S}(x) \equiv D \sum_{\alpha=1}^{6} \mathcal{G}(e_\alpha, x) = \mathcal{G}^0(0, x)/0, 0). \tag{B3}$$

At $\varepsilon \to 0$, the GF $\mathcal{G}^0(0, x)$ can be expanded as a series in $\sqrt{\varepsilon}$, namely $a_0(x) + a_1(x)\sqrt{\varepsilon} + \ldots$. Thus (B3) has the Laplace original $\approx t^{-3/2}$ at $t \to \infty$. The case $x = 0$ is described separately, giving, in view of (56b), $\bar{S}(0) = 0$.

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