CHEMICAL KINETICS AND CATALYSIS

Kinetic Equations of Physicochemical Processes with Allowance for Multi-Particle Effects in the Lattice Gas Model

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Abstract—A way of deriving kinetic equations of physicochemical processes in dense phases is developed on the basis of the discrete–continuous description of the spatial distribution of components in the lattice gas model (LGM), with allowance for multi-particle effects. The emergence of multi-particle effects is associated with the simultaneous influence of all neighbors on the rate of the elementary stage with the participation of a given particle. They include multi-particle potentials of interaction, including quantum–chemical energy calculations, the effect the configurations of neighboring molecules have on the internal motion of the central particle, and the effects of the indirect correlation of interacting particles that occurs for any potential of pair interaction, assuming the internal motions of particles do not depend on the local configurations of neighbors. Multi-particle effects take models beyond the quasi-chemical approximation, which reflects direct correlations of interacting particles through pair distribution functions, and require the use of correlation functions for a larger number of particles in describing their kinetics. The rates of elementary one- and two-node stages are calculated within the theory of absolute rates of reactions in non-ideal reaction systems. Ways of calculating approximate rates of the elementary stages of mono- and bimolecular processes are discussed, along with the possibilities of generalizing the derived equations.

Keywords: kinetic equations, dense phase processes, multi-particle effects, lattice gas model, non-ideal reaction systems

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INTRODUCTION

The development of a new associative model of the liquid state [1] has revealed a number of questions in the statistical theory of the condensed state that failed earlier to receive the attention they deserve [1]. Intermolecular pair interaction potentials of components are renormalized into multi-particle potentials under the effect of anharmonic vibrations in bound associates. This results in effective multi-particle potentials that depend on the temperature and concentrations of components. The emergence of effective potentials dependent on temperature and density has long been known from the theory of metal melts [2] and the theory of fluids [3]. We are referring here to effective pair potentials obtained by averaging over the spatial distribution of interacting particles without considering the effects of their vibrations. Directly allowing for vibrations produces effective multi-particle potentials. The effect intermolecular interaction has on the frequencies of interparticle vibration changes the average distance between neighboring particles, along with the depth of the potential well and its curvature near the minimum. A change in energy alters the rates of elementary reactions in liquid phases and their concentration dependences.

The associative fluid model was formulated on the basis of the discrete–continuous description of the spatial distribution of components in the LGM [4–6]. This theory corresponds to the best developed approach to many of the physicochemical processes in condensed phases that occur in three aggregate states, including large homogeneous [7–15] and numerous heterogeneous systems [13–24]. Apart from situations with spatial phase separation (the formation of heterogeneous systems), these can contain systems with different spatial matrices formed by one component, and between which other components can locate. These systems contain, e.g., solid porous and non-porous adsorbents (membranes) that absorb vapor or fluid molecules; solid absorbents that absorb atoms, ions, and molecules from other phases into their interstitial sites; and the dissolution of diverse mixtures in complex dispersion phases.

The modern kinetic theory of condensed phases is based on that of absolute reaction rates of non-ideal systems [6, 25]. Strictly speaking, multi-particle effects arise automatically in kinetics due to the simultaneous effect all neighboring molecules have on the rate of the elementary stage with the participation of the relevant central particle. The central particle can

be single when the stage proceeds at one site (monomolecular stages) or two particles when it proceeds in two neighboring sites (bimolecular stages).

Due to the simultaneous effect of all neighbors of the central reagents, the rate of the elementary stage depends on the state of the entire multi-particle configuration formed by the central particle and its neighbors. The interaction between them form a reaction cluster and the local activation energy of the stage. The rate depends on the approximation used when considering interparticle interaction. The theory most widely accepted today uses the so-called quasi-chemical approximation (QCA) with allowance for direct correlations between interacting particles [6, 19]. This approximation provides a self-consistent description of equilibrium and kinetics when considering the pair interaction potential between components, so long as the internal motions of molecules in LGM cells are independent of the configurations of neighbors.

The aim of this work is to extend this theory to considering multi-particle effects for a discrete description of the spatial distribution of components in the LGM. It should be noted that apart from the above associative fluid model, multi-particle effects also emerge when different types of multi-particle interaction potentials are used, including quantum-chemical calculations of a system's energy (with optimization of the geometry of complexes [26, 27]), and in the familiar means of the liquid state theory (integral equations) that describe indirect correlations. Integral equations underlie the current theory of the liquid state described by correlation functions (CFs) with a wide spectrum of interaction potentials [3, 4, 28, 29]. The same CFs are used in discrete interpretations of the LGM [30–32]. The need for more detailed consideration of contributions from different molecular configurations, rather than simply allowing for pair contributions from interacting particles, is common to the above situations.

The procedure for deriving kinetic equations for the above mono- and bimolecular elementary stages in condensed phases was developed in [6, 25, 33–37]. In this work, we go beyond the pair description of correlation effects, which alters the structure of kinetic equations and ways of calculating approximate rates of elementary stages. Multi-particle effects take models beyond the use of the QCA by employing pair CFs and requiring them for a larger number of particles in describing kinetics (below, we use the term correlator in addition to the abbreviation CF). It should also be noted that initial logic of using CFs to describe the full set of local particle configurations remains the same [6, 19, 33–37]. The change in LGM parameters when considering multi-particle effects uses the same set of configurations, so the way in which relationships between CFs are constructed is not altered.

Below, we formulate a model that describes interactions with nearest neighbors in the cluster approach

(CA) [6, 19, 33, 37–39]. The CA introduces correlators of the first and second types. The first type of correlators has a simple relationship with the local energy of the system, and all thermodynamic functions are expressed through correlators of the second type. Kinetic equations are deduced for correlators of the second type, and the rates of elementary stages are expressed via correlators of the first type. The structure of kinetic equations is derived below without considering the multi-particle parameters of the LGM. Specific features of deriving new kinetic equations are discussed. General expressions for the rates of the elementary steps of mono- and bimolecular stages are then considered, along with proof of the self-consistency of the derived expressions for forward and backward one- and two-node stages with an equilibrium description of the reaction systems. We then discuss ways of approximating expressions for the rates of elementary stages under the condition of local equilibrium, along with the relationship between calculations of the derived rates of elementary stages and thermodynamic functions of the system beyond the QCA.

MODEL AND CORRELATION FUNCTIONS

In the LGM, system volume V is divided into cells about the size of a molecule (v_0). Each cell is numbered with index f , where $1 \leq f \leq M$; and $M = V/v_0$ is the number of cells in the system. The occupancy of each site is characterized by value γ_f^i . If site f is occupied by a molecule of type i , $\gamma_f^i = 1$. If the site contains another type of molecule, $\gamma_f^i = 0$. The number of components in the system is s , and $1 \leq i \leq s$. The γ_f^i values satisfy conditions (1) $\sum_{i=1}^s \gamma_f^i = 1$ and (2) $\gamma_f^i \gamma_f^j = \Delta_{ij} \gamma_f^i$, where Δ_{ij} is the Kronecker delta. These two conditions mean that each cell (or site) is occupied by a molecule of only one kind.

Let the lattice structure have z nearest neighbors. For simplicity in considering the interaction between molecules, we limit ourselves to the distance of the nearest neighbors. We must consider the multi-particle parameters of the LGM, which include the occurrence of multi-particle interaction potentials and the effect different configurations of neighboring molecules have on the internal motions of molecules.

The total energy of the system (Hamiltonian H) is written [6] as the sum over all sites of the system: $H = \sum_{f,i} h_f^i(K_1)$, where $h_f^i(K_1)$ is the Hamiltonian for cluster K_1 consisting of one central site f and its z nearest neighbors $g_1 \dots g_z$, with summands of two types of contributions from the internal motion of molecule i

in cell f ($v_f^i(K_1) = v_{fg_1 \dots g_z}^{ij_1 \dots j_z}$) and its interaction with neighbors ($\epsilon_{fg_k}^{ij_k}(K_1) = \epsilon_{fg_k \{j_1 \dots j_z\}}^{ij_k}$):

$$h_f^i(K_1) = \sum_{k=1}^z \sum_{j_k=1}^s [v_f^i(K_1) - \epsilon_{fg_k}^{ij_k}(K_1)] \gamma_f^i \Gamma_{\{g\}}^{(j)}(K_1) \quad (1)$$

$$= \left[v_f^i(K_1) - \sum_{k=1}^z \sum_{j_k=1}^s \epsilon_{fg_k}^{ij_k}(K_1) \right] \gamma_f^i \Gamma_{\{g\}}^{(j)}(K_1),$$

where symbol $\epsilon_{fg_k}^{ij_k}(K_1)$ for the parameter of multi-particle interaction retains the meaning of the bond between central particle i in cell f and j_k in cell g_k , with $1 \leq k \leq z$. However, the energy of the pair bond is modified by the effect of the other neighbors from $g_{k=1}$ to $g_{k=z}$, excluding given site g_k . The sum in (1) is taken over all neighbors $g_1 \dots g_z$ containing particles $j_1 \dots j_z$, respectively. Here, we give abbreviated relation $\Gamma_{\{g\}}^{(j)}(K_1) = \gamma_{g_1}^{j_1} \dots \gamma_{g_z}^{j_z}$. In other words, the states of occupancy for neighboring particles $j_1 \dots j_z$ change on a cluster with fixed central molecule i in all neighboring sites $g_1 \dots g_z$. The total number of K_1 cluster configurations is s^{1+z} .

We use the grand canonical ensemble to describe equilibrium. Chemical potential μ_i of molecule i is included on the $v_f^i(K_1)$ value: $v_f^i(K_1) = -(\beta^{-1} \ln Q_f^i(K_1) + \mu_i + E_f^i(K_1))$, where $E_f^i(K_1)$ is the potential of a lattice system at site f , and $Q_f^i(K_1)$ is the statistical sum of molecule i in a dense phase. For the chemical potential in the gas phase, $\mu_i = \mu_i^0 + \beta^{-1} \ln[\beta P_i / Q_i^0]$, where μ_i^0 is the reference point of the former: $\mu_i^0 = 0$ for a free particle in the gas phase or $\mu_i^0 = \epsilon_i$ in the ad- or absorbed state, and $\beta = (k_B T)^{-1}$. Here, P_i is the partial pressure of molecule i . The $v_f^i(K_1)$ value reflects the ratio of the statistical sum of molecule i in cell f of the lattice system, and in the gas phase:

$$v_f^i(K_1) = -kT \ln[Q_f^i(K_1) \beta P_i \exp[\beta E_f^i(K_1)] / Q_i^0] \quad (2)$$

$$= -\beta^{-1} \ln[a_f^i(K_1) P_i],$$

where $a_f^i(K_1) = Q_f^i(K_1) \beta \exp[\beta E_f^i(K_1)] / Q_i^0$ is the local constant of retention (for problems of adsorption and absorption, this is the Henry constant at an additional non-zero potential $E_f^i(K_1)$ of an ad- or absorbent) of particle i in cell f ; and $Q_i^0 = Q_{i \text{ tran}}^0 Q_{i \text{ rot}}^0 Q_{i \text{ vib}}^0$ is the statistical sum of a particle in gas. A similar relation of internal motions is given for the motion of component i in a dense phase:

$$Q_f^i(K_1) = Q_f^i(K_1)_{\text{tran}} Q_f^i(K_1)_{\text{rot}} Q_f^i(K_1)_{\text{vib}}.$$

In the CA used to derive equations for the equilibrium distribution of components, we use two types of correlators [6, 38] to avoid finding the statistical weights of individual configurations in the statistical sum of system Q . Correlators of the first type distinguish local energy characteristics of configurations, while those of the second type are needed to calculate the thermodynamic characteristics of the system. The first correlator of the second type is thus related to local partial occupancies θ_i of system sites and/or chemical potential (isotherm) μ_i . The second correlators represent probabilities θ_{ij} of the presence of particles i and j in neighboring lattice sites, through which we can determine, e.g., heats of sorption or mixing, heat capacities, and activity coefficients. Introducing two types of correlators allows us to reduce deriving a set of equations for correlators of the second type to an operation using the ratios of their probability (instead of determining the statistical weights of configurations).

Correlators of the first type are defined through cluster Hamiltonians (1) as

$$\theta_{fg_1 \dots g_z}^{ij_1 \dots j_z} = \langle \gamma_f^i \Gamma_{\{g\}}^{(j)} \rangle = \langle \gamma_f^i \gamma_{g_1}^{j_1} \dots \gamma_{g_z}^{j_z} \rangle$$

$$= \frac{\text{const}(j_1 \dots j_z)}{Q} \exp \beta \left[-v_f^i(K_1) + \sum_{k=1}^z \sum_{j_k=1}^s \epsilon_{fg_k}^{ij_k}(K_1) \right]. \quad (3)$$

Exponent (3) contains a cluster local internal energy for a particular configuration $ij_1 \dots j_z$ of cluster K_1 . The ratio of correlators of the first type with different central sites allows us to exclude unknown constant $\text{const}(j_1 \dots j_z)$ and the statistical sum of system Q , which gives

$$\theta_{fg_1 \dots g_z}^{Aj_1 \dots j_z} / \theta_{fg_1 \dots g_z}^{Bj_1 \dots j_z} = \exp \beta \left[v_f^B(K_1) - v_f^A(K_1) \right. \quad (4)$$

$$\left. + \sum_{k=1}^z \sum_{j_k=1}^s (\epsilon_{fg_k}^{Aj_k}(K_1) - \epsilon_{fg_k}^{Bj_k}(K_1)) \right] = M_{f\{g_1 \dots g_z\}}^{AB\{j_1 \dots j_z\}}.$$

Formula (4) determines the pair relationship between correlators of the first type with identical states of all neighbors $j_1 \dots j_z$ through local energies of a cluster with different occupancy states of central sites A and B .

Correlators of the second type are obtained from correlators of the first type by averaging over the occupancy states of some of the nearest sites. They are defined as

$$\theta_{fg_1 \dots g_n}^{ij_1 \dots j_n} = \langle \gamma_f^i \gamma_{g_1}^{j_1} \dots \gamma_{g_n}^{j_n} \rangle, \quad 0 \leq n \leq z. \quad (5)$$

The relation for correlators of the first and second types is written as

$$\theta_{fg_1 \dots g_n}^{ij_1 \dots j_n} = \langle \gamma_f^i \gamma_{g_1}^{j_1} \dots \gamma_{g_n}^{j_n} \rangle = \sum_{j_{n+1}} \dots \sum_{j_z} \theta_{fg_1 \dots g_z}^{ij_1 \dots j_z}. \quad (6)$$

On the right, summation is done over the occupancy states of $j_{n+1} \dots j_z$ sites that are missing from subscripts of the correlator on the left.

To derive equations for the equilibrium distribution of components we must associate correlators of the second type derived for different central particles [6, 38]. The need to move to relationships between correlators of the second type with different central sites is due to all approximations being constructed through correlators of the second type. By substituting Eq. (4) in the right side of (6) for central component $i = A$ expressed through central component B , we have the relation

$$\theta_{f_{g_1 \dots g_n}}^{A j_1 \dots j_n} = \sum_{j_{n+1}} \dots \sum_{j_z} \theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z} M_{f \{j_1 \dots j_z\}}^{AB}, \quad (7)$$

in which correlators of the second type with center A are expressed through correlators of the first type with center B .

Subsequent derivation of equations for the equilibrium distribution of components requires substituting correlator of the first type $\theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z}$ in (7) for correlators of the second type with the same central particle B ($\theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z} = \theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z}(\{\theta_{f_{g_1 \dots g_n}}^{B j_1 \dots j_n}\})$). After finding relation $\theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z} = \theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z}(\{\theta_{f_{g_1 \dots g_n}}^{B j_1 \dots j_n}\})$, they are substituted into the right side of the set of Eqs. (7), producing the sought expression for correlators of the second type with different central components: On the left, there is a correlator of the second type with center A ; on the right, there is a correlator of the second type with center B .

To find relation $\theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z} = \theta_{f_{g_1 \dots g_z}}^{B j_1 \dots j_z}(\{\theta_{f_{g_1 \dots g_n}}^{B j_1 \dots j_n}\})$, we must move from the coordinate description of the distribution of neighbors in different configurations (5) and (6) to their energy contributions from particles of different kinds. If we use the description of configurations of $j_1 \dots j_z$ neighbors through numbers of bonds n_{ij} between center i and a neighbor of the j type, we can rewrite formula (6) for particular configurations by grouping correlators of the first type with fixed numbers n_{ij} (configurations with at least n_{ij} neighbors of the j type in this case correspond to correlators of the second type) [6, 38]:

$$\theta_{n_1 \dots n_{s-1}}^B = \sum_{k_1=0}^{\tilde{z}} \dots \sum_{k_{s-1}=0}^{\tilde{z}-\tilde{k}} b_{\sigma(\{n+k\})}^{\sigma(\{n\})} \theta_{n_1+k_1, \dots, n_{s-1}+k_{s-1}}^B, \quad (8)$$

where the upper limits of the sums are defined as $\tilde{z} = z - n_1 - \dots - n_{s-1}$, $\tilde{k} = k_1 + \dots + k_{s-1}$. Here, $b_{\sigma(\{n+k\})}^{\sigma(\{n\})}$ are the numbers of transitions of correlators of the first type needed to obtain a correlator of the second type with dimensionality n . Symbol $\sigma(\{n\})$ denotes the arrangement the number of particles $\{n\} = n_1, \dots, n_{s-1}$ (the braces signify the full set of types), as does symbol $\sigma(\{n+k\})$ corresponding to neighboring particles of different kinds around central particle B . Symbol $\sigma(\{n\})$ is of a vector nature in a multicomponent system.

Inverting the set of Eq. (8) gives expressions for correlators of the first type through correlators of the second type:

$$\theta_{n_1 \dots n_{s-1}}^B = \sum_{k_1=0}^{\tilde{z}} \dots \sum_{k_{s-1}=0}^{\tilde{z}-\tilde{k}} (-1)^{k_1 + \dots + k_{s-1}} \times \sum_{\sigma(\{n_1+k_1\})} b_{\sigma(\{n+k\})}^{\sigma(\{n\})} \theta_{n_1+k_1, \dots, n_{s-1}+k_{s-1}}^B. \quad (9)$$

Derived relation (9) is substituted into the right side of the set of Eqs. (7), producing the sought expression for correlators of the second type with different central components, which describes their equilibrium distribution. This set of equations reflects multi-particle effects and covers all configurations of neighbors. It is therefore cumbersome.

As the simplest example, let us illustrate the use of symbols σ in a binary system (particles A and B) when the arrangement of neighbors is clearly associated with irreducible configurations of neighbors [6, 25]. If we omit the subscript of site numbers, and instead denote through n the number of components A among z neighbors around central particle $i = A$ and B , instead of expressions (6) and (8), we have

$$\theta_{n,\sigma}^i = \sum_{k=0}^{z-n} \sum_{\sigma(n+k)} b_{\sigma(n+k)}^{\sigma(n)} \theta_{n+k,\sigma}^i, \quad \sum_{\sigma(n+k)} b_{\sigma(n+k)}^{\sigma(n)} = C_{z-n}^k, \quad (10)$$

where sum $\sigma(n+k)$ is taken over all possible configurations at a given number of particles A ($n+k$) that occur as they are added to configuration $\sigma(n)$: $\sum_{\sigma(n+k)} b_{\sigma(n+k)}^{\sigma(n)} = C_{z-n}^k$, $C_m^k = m!/[k!(m-k)!]$ is the number of combinations. The right side of Eq. (10) contains correlators with brackets in subscripts, which correspond to correlators of the first type with a fixed number of particles A and their arrangement.

Using the CA [6, 39] when considering multi-particle LGM parameters for a binary mixture, we obtain the following expression for the equilibrium distribution of components (only $E_i(n\sigma) = \sum_{k=1}^z \varepsilon_{f_{g_k}\{j_1 \dots j_z\}}^{ij_k\{j_1 \dots j_z\}}$ was considered earlier):

$$\theta_{n,\sigma}^A = \sum_{k=0}^{z-n} \sum_{\sigma(n+k)} b_{\sigma(n+k)}^{\sigma(n)} M_{n+k,\sigma}^{BA} \theta_{n+k,\sigma}^B, \quad (11)$$

$$M_{n,\sigma}^{BA} = \exp \beta [v_B(n\sigma) - v_A(n\sigma) + E_A(n\sigma) - E_B(n\sigma)],$$

where in, e.g., the QCA, $\theta_{[n]}^A = \theta_A(t_{AA})^k (t_{AB})^{z-k}$, where $t_{AA} = \theta_{AA}/\theta_A$ is the conventional probability of one particle A being near another particle A ; θ_A is the concentration of component A ; and θ_{AA} is the probability of two particles A being in neighboring sites.

Multi-particle effects generally require the use of numerical calculations in which deriving the coefficients of $b_{\sigma(n+k)}^{\sigma(n)}$ is a not complicated procedure.

Correlators of the second type with different dimensionalities are related to one another by normalization conditions that are satisfied for any characteristic time scales τ :

$$\theta_{f_1 \dots f_m}^{i_1 \dots i_m}(\tau) = \sum_{i_{m+1}=1}^s \theta_{f_1 \dots f_m f_{m+1}}^{i_1 \dots i_m i_{m+1}}(\tau), \quad \sum_{i=1}^s \theta_f^i(\tau) = 1. \quad (12)$$

Correlators (12) characterize the probability of a cluster consisting of m particles, in which a particle of type i_n is at a site with number f_n at time τ ; $1 \leq n \leq m$, where m is the dimensionality of the correlator.

KINETIC EQUATIONS FOR CORRELATORS

The evolution of the system is described by kinetic equations for correlators of the second type with different dimensionality. The approach to deriving kinetic equations in the LGM was developed in [6, 37, 40]. Let the considered process consist of many stages, and we denote by α the number of the stage of the elementary process.

Let us denote through $\{I\} = \{\gamma_{f_n}^i\} = \gamma_{f_1}^{i_1} \dots \gamma_{f_M}^{i_M}$ the total set (or the full list) of γ_f^i angle values of all sites of lattice M , $1 \leq i_n \leq s$, which unambiguously define the total configuration of particle arrangements on the lattice at time τ . Kinetic equations for correlators of the system upon moving from initial state $\{I\}$ to final state $\{II\}$ are written as

$$\frac{d}{d\tau} \theta_{f_1 \dots f_m}^{i_1 \dots i_m}(\tau) = \sum_{\alpha, \{II\}} \left[\prod_{n=1}^m \gamma_{f_n}^{i_n} W_{\alpha}(\{II\} \rightarrow \{I\}) - \prod_{n=1}^m \gamma_{f_n}^{i_n} W_{\alpha}(\{I\} \rightarrow \{II\}) \right], \quad (13)$$

where particle types i_n^* in the first summand on the right side correspond to the occupancy states of lattice sites in final state $\{II\}$. Here, $W_{\alpha}(\{I\} \rightarrow \{II\})$ is the probability of elementary process α occurring, with the system moving from initial state $\{I\}$ to final state $\{II\}$ by time τ as a result. In formula (13), the sum is taken over different kinds of direct processes (index α) and all inverse processes $\{II\}$ in which the occupancy state of each site of the system changes.

Probabilities of transitions $W_{\alpha}(\{I\} \rightarrow \{II\})$ in Eq. (13) obey the condition of detailed equilibrium $W_{\alpha}(\{I\} \rightarrow \{II\}) \exp(-\beta H(\{I\})) = W_{\alpha}(\{II\} \rightarrow \{I\}) \exp(-\beta H(\{II\}))$, where $H(\{I\})$ is the total energy of a lattice system in state $\{I\}$. Equation (13) and probabilities of transitions W_{α} are traditionally written in the Mark approximation, where it is assumed that relaxation of the internal degrees of freedom of all particles proceeds more rapidly than changes in the occupancy states of different sites of a lattice system. This condition is modified in the associative fluid model so that the internal states of molecules with different numbers

of neighbors are identified according to the number of neighbors and their arrangement (which determine their multi-particle character). The internal degrees of freedom $Q_f^i(K_1)$ of a molecule of type i in (13) thus depend on the configurations of neighbors.

Equations (13) are the start for obtaining kinetic equations of processes that occur in condensed phases. In the right side of the kinetic equation for the local concentration of molecules (where $\theta_f^i = \langle \gamma_f^i \rangle$ are first order correlators (12) and $m = 1$) has summands $U_f^i(\alpha)$ for the rates of elementary one-site processes $i \leftrightarrow b$ (where $h \in z_f$), and $U_{fg}^{ij}(\alpha)$ for the rates of elementary two-site processes $i + j_{\alpha} \leftrightarrow b + d_{\alpha}$ ($h \in z$) in the nearest f and g sites [6, 29, 32]:

$$\frac{d}{dt} \theta_f^i = I_f^i = \sum_{\alpha} [U_f^b(\alpha) - U_f^i(\alpha)] + \sum_h \sum_j \sum_{\alpha} [U_{fh}^{bd}(\alpha) - U_{fh}^{ij}(\alpha)]. \quad (14)$$

These summands contain higher order CFs than the first, and Eq. (14) cannot be closed without losing the correlation effects.

The next equation of the system for pair correlators $(\theta_{fg}^{ij}) = \langle \gamma_f^i \gamma_g^j \rangle$ is written as

$$\begin{aligned} \frac{d}{dt} \theta_{fg}^{ij} &= I_{fg}^{ij} = \sum_{\alpha} [U_{fg}^{bd}(\alpha) - U_{fg}^{ij}(\alpha)] + P_{fg}^{ij} + P_{gf}^{ji}, \\ P_{fg}^{ij} &= \sum_{\alpha} [U_{fg}^{(b)j}(\alpha) - U_{fg}^{(i)j}(\alpha)] \\ &+ \sum_h \sum_m \sum_{\alpha} [U_{hfg}^{(cb)j}(\alpha) - U_{hfg}^{(mi)j}(\alpha)], \end{aligned} \quad (15)$$

where the second summand in P_{fg}^{ij} describes stage $i + m \leftrightarrow b + c$ in neighboring f and h sites. Equations (15) contain summands $U_{fg}^{(i)j}(\alpha)$ and $U_{hfg}^{(mi)j}(\alpha)$ corresponding to one- ($i \leftrightarrow b$) and two-site ($i + m \leftrightarrow b + c$) reactions of particle i with neighboring particle j . However, particle j does not participate in elementary process α itself; rather, it changes the activation barrier for reacting particle i in the one-site stage and reacting particles i and m in the two-site stage.

As an example, we present the explicit form of kinetic equations for the first two correlators of a binary system in which there is the first stage of non-dissociative adsorption–desorption ($\alpha = 1$), and jumps of particle A to neighboring vacancies V ($\alpha = 2$)

$$\begin{aligned} \frac{d}{dt} \theta_f^A &= I_f^A = [U_f^V(1) - U_f^A(1)] \\ &+ \sum_{h \in z_f} [U_{fh}^{VA}(2) - U_{fh}^{AV}(2)]. \end{aligned} \quad (16)$$

The first brackets correspond to the one-site stage of adsorption–desorption on the central f site (sum-

mand $U_f^A(1)$ describes the desorption stage), and the second brackets (symbol (2) corresponds to jumps, $j = A, V$; $h \in z_f$) describes the stage of the A particle jump from the central f site to site h ($U_{fh}^{AV}(2)$) and vice versa. The θ_f^V value is found from normalization condition (12).

The equation of a system for pair CF is written as

$$\frac{d}{dt}\theta_{fg}^{AA} = I_{fg}^{AA} = [U_{fg}^{(V)A}(1) - U_{fg}^{(A)A}(1)] + [U_{fg}^{A(V)}(1) - U_{fg}^{A(A)}(1)] + P_{fg}^{AA} + P_{gf}^{AA}. \quad (17)$$

Reacting particle A or V is identified in the superscript in parentheses. The first two brackets correspond to the one-site stage of adsorption–desorption in central f and g sites. The second particle of the pair (the superscript without parentheses) affects the course of the process, but the occupancy state of the site with this particle does not change. Third summand P_{fg}^{AA} corresponds to jumps of particle A from site f to neighboring vacant sites h , $h \in z_f^*$; symbol z_f^* means there is no site g with neighboring particle A among the nearest neighbors of site f . $P_{fg}^{AA} = \sum_{h \in z_f^*} [U_{hfg}^{(AV)A}(2) - U_{hfg}^{(VA)A}(2)]$. The fourth summand has a similar form: particle A at site g exchanges h with its neighbors, $h \in z_f^*$, around site g , except for site f : $P_{gf}^{AA} = \sum_{h \in z_g^*} [U_{fgh}^{A(VA)}(2) - U_{fgh}^{A(AV)}(2)]$.

Pair CFs have normalization relations for the occupancy states of both first site f and second site g : $\theta_{fg}^{AA} + \theta_{fg}^{AV} = \theta_f^A$, $\theta_{fg}^{VA} + \theta_{fg}^{VV} = \theta_f^V = 1 - \theta_f^A$. Note that to describe the evolution of pair CFs it is not enough to know one pair function θ_{fg}^{AA} if $\theta_{fg}^{AV} \neq \theta_{fg}^{VA}$ (e.g., there is the density gradient along the line/axis passing through fg). We also need the second equation for pair CFs in, e.g., the form

$$\begin{aligned} \frac{d}{dt}\theta_{fg}^{AV} = I_{fg}^{AV} = & [U_{fg}^{(V)V}(1) - U_{fg}^{(A)V}(1)] \\ & + [U_{fg}^{A(A)}(1) - U_{fg}^{A(V)}(1)] + [U_{fg}^{VA}(2) - U_{fg}^{AV}(2)] \\ & + P_{fg}^{AV} + P_{gf}^{VA}. \end{aligned} \quad (18)$$

The first two summands have the same meaning as in Eq. (17): they are elementary stages at sites f and g , and they have a fixed state of particle A at site f and vacancy V at site g . The third summand describes the particle exchange at the central pair of sites fg (superscripts have no parentheses, since both particles participate in the stage). The last two summands have the structure of expressions P_{fg}^{AA} and P_{gf}^{AA} :

$$P_{fg}^{AV} = \sum_{h \in z_f^*} [U_{hfg}^{(AV)V}(2) - U_{hfg}^{(VA)V}(2)]$$

and

$$P_{gf}^{VA} = \sum_{h \in z_g^*} [U_{fgh}^{A(AV)}(2) - U_{fgh}^{A(VA)}(2)].$$

KINETIC EQUATIONS FOR HIGHEST CORRELATORS

In the QCA, pair correlators describe only direct correlations of interacting particles. To consider indirect correlations along with multi-particle effects, we must move to the equations of system (13) with large correlators. In Eqs. (14) and (15), the dimensionality of correlators on the right is larger than that of correlators on the left [6, 25, 37, 40]. This dimensionality equals the number of all neighboring molecules that simultaneously affect the rate of this stage. The minimum dimensionality of the correlator in (14) is the dimensionality of reaction cluster $K_1 = 1 + z$ for one-site stages (for two-site stages, the dimension of the reaction cluster is around $K_2 = 2z$). We recall that in Bogolyubov's kinetic hierarchy [41], the dimensionality of correlators in the right side of kinetic equations grows in steps of 1. This differentiates the structure of LGM kinetic equations from the traditional form of kinetic equations of Bogolyubov's hierarchies [41–44], and the problem of the self-consistent calculation of high dimensionality correlators up to the K_1 dimension arises in the kinetic theory. Aspects of the procedure for deriving kinetic equations for highest correlators is can be discussed using the example of a triple correlator in a binary system.

Triple correlator θ_{fgh}^{AAA} is the first correlator that describes indirect correlations. As above, we let the kinetic equation for its evolution also be formed in two types of stages: adsorption–desorption ($\alpha = 1$) and jumps to the neighboring sites ($\alpha = 2$)

$$\frac{d}{dt}\theta_{fgh}^{AAA} = I_{fgh}^{AAA} = I_{fgh}^{AAA}(1) + I_{fgh}^{AAA}(2). \quad (19)$$

Here, first summand $I_{fgh}^{AAA}(1)$ reflects the contributions from one-site adsorption and desorption process at sites fgh (three parentheses describe the participation of particles A in different sites fgh in this triple correlator)

$$\begin{aligned} I_{fgh}^{AAA}(1) = & [U_{fgh}^{(V)AA}(1) - U_{fgh}^{(A)AA}(1)] \\ & + [U_{fgh}^{A(V)A}(1) - U_{fgh}^{A(A)A}(1)] + [U_{fgh}^{AA(V)}(1) - U_{fgh}^{AA(A)}(1)]. \end{aligned} \quad (20)$$

Second summand $I_{fgh}^{AAA}(2)$ in (19) describes jumps. The three central sites contain only particles A , so direct exchange between them as in Eq. (18) is impossible. The second summands in (19) have the structure $I_{fgh}^{AAA}(2) = P_{fgh}^{AAA} + P_{gfh}^{AAA} + P_{hfg}^{AAA}$. As above, the first

superscript corresponds to particle A exchanged with its neighbors; $P_{fgh}^{AAA} = \sum_{\xi} [U_{\xi fgh}^{(AV)AA} - U_{\xi fgh}^{(VA)AA}]$, and the parentheses in the superscripts indicate at which sites $f\xi$ jumps take place. The potential of other particles A at sites gh affect the rate of the elementary jump stage between sites $f\xi$, but they remain in their sites. Similarly, $P_{gfh}^{AAA} = \sum_{\xi} [U_{\xi gfh}^{(AV)AA} - U_{\xi gfh}^{(VA)AA}]$ and $P_{hfg}^{AAA} = \sum_{\xi} [U_{\xi hfg}^{(AV)AA} - U_{\xi hfg}^{(VA)AA}]$.

The triple correlator has four conditions of normalization (12), $\sum_{k=A,V} \theta_{f_1 f_2}^{kij}(\tau) = \theta_{f_1 f_2}^{ij}(\tau)$, which associate them with four pair CFs, $\theta_{f_1 f_2}^{ij}$, $ij = AA, AV, VA, VV$.

This means that in addition to the equation for triple correlator (19), there must be other kinetic equations containing one and two vacancies in the superscripts:

$$\frac{d}{dt} \theta_{fgh}^{AAV} = I_{fgh}^{AAV} = I_{fgh}^{AAV}(1) + I_{fgh}^{AAV}(2) \quad (21)$$

and

$$\frac{d}{dt} \theta_{fgh}^{AVV} = I_{fgh}^{AVV} = I_{fgh}^{AVV}(1) + I_{fgh}^{AVV}(2).$$

The structure of these summands is written as when moving from (17) to (18). In addition to jumps from neighboring sites ξ , there are summands with direct jumps between the central sites for each of three types of correlators at sites fgh . For θ_{fgh}^{AAV} the $I_{fgh}^{AAV}(1)$ and $I_{fgh}^{AAV}(2)$, summands are written as

$$I_{fgh}^{AAV}(1) = [U_{fgh}^{(V)AA}(1) - U_{fgh}^{(A)AA}(1)] + [U_{fgh}^{(A(V)A)}(1) - U_{fgh}^{(A(A)A)}(1)] + [U_{fgh}^{AA(A)}(1) - U_{fgh}^{AA(V)}(1)]. \quad (22)$$

Here, one-site stages occur in three sites fgh of the correlator. The character of the arrangement of sites fgh is important for contributions from the summands with jumps. For instance, the three neighboring sites in square lattice ($z=4$, $d=2$) can be either on one line or form an angle, so sites f and h cannot be nearest sites. We therefore have one jump between sites g and h for $z=4$:

$$I_{fgh}^{AAV}(2) = [U_{fgh}^{A(VA)}(2) - U_{fgh}^{A(AV)}(2)] + P_{fgh}^{AAV} + P_{gfh}^{AAV} + P_{hfg}^{AAV}, \quad (23)$$

while for planar hexagonal lattice ($z=6$, $d=2$) three sites can be nearest ones. This results in the second summand in $I_{fgh}^{AAV}(2)$:

$$I_{fgh}^{AAV}(2) = [U_{fgh}^{A(VA)}(2) - U_{fgh}^{A(AV)}(2)] + [U_{gfh}^{A(VA)}(2) - U_{gfh}^{A(AV)}(2)] + P_{fgh}^{AAV} + P_{gfh}^{AAV} + P_{hfg}^{AAV}. \quad (24)$$

In both cases, the three last summands in the expressions describe the exchange between particles A

and neighboring vacancies (i.e., they provide an expansion of the dimensionality of correlators, along with the effect of the lateral interaction potential):

$$P_{fgh}^{AAV} = \sum_{\xi} [U_{\xi fgh}^{(AV)AV} - U_{\xi fgh}^{(VA)AV}],$$

$$P_{hfg}^{AAV} = \sum_{\xi} [U_{\xi hfg}^{(AV)AV} - U_{\xi hfg}^{(VA)AV}], \quad \text{etc.}$$

The same procedure is used in the successive increase in correlator dimensionality n at sites $(f_1 f_2 \dots f_n)$. Below, we present the structure of kinetic equations in the general form only for particles A and the vacancies among them (occupancy states of correlators of dimensionality n at sites $f_1 f_2 \dots f_n$ are denoted as $i_1 i_2 \dots i_n$)

$$\frac{d}{dt} \theta_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n} = I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n} = I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(1) + I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(2), \quad (25)$$

$$I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(2) = U_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(2) + P_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}.$$

The presented structure of set of kinetic equations (25) assumes the additional use of $n(s-1)$ normalizations (12) for correlators with dimensionality n and different numbers of vacancies in the superscripts. The system contains contributions from one-site stages $I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(1)$ and particle jumps to vacant sites $I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(2)$, which grow along with n . These jumps occur at both sites of this correlator with dimensionality n (summand $U_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}(2)$) and sites of the correlator with dimensionality $(n+1)$ (summand $P_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}$).

This set of equations for adsorption of a non-dissociating molecule can be easily rewritten for dissociative adsorption—desorption when the elementary stage proceeds at two neighboring sites. All summands from stage $\alpha=1$ at one site in this case disappear. In their place emerge summands from stage $\alpha=1$ at two sites. The principle of deriving the kinetic equations is retained for multicomponent mixtures and the growing number of elementary stages α , but the system becomes much more cumbersome.

To close the equations for correlators we need the explicit form of expressions for the rates of elementary one- and two-site stages that occur in reaction clusters with sizes $K_1 = 1+z$ and $K_2 = 2z$. All rates of the elementary stages in dense phases $U_f^i(\alpha)$ and $U_{fg}^{ij}(\alpha)$ are calculated using the theory of the absolute rates of reactions in non-ideal reaction systems [6, 25, 33–36].

RATES OF ONE-SITE STAGES

In the transitional state, an activated complex (AC) interacts with neighboring particles. The multi-particle parameter of interaction between the AC and neighbors ($\varepsilon_{fg_k}^{*ij_k}(K_1) = \varepsilon_{fg_k\{g_1 \dots g_z\}}^{*ij_k\{j_1 \dots j_z\}}$) formed by particle A

with neighboring particles $j_1, \dots, j_z$ at sites $g_1, \dots, g_z$ differing from parameter of interaction $\varepsilon_{fg_k}^{A_{jk}}(K_1)$ between initial reagent i from which the AC is formed and neighboring particle j . When there is no AC of one-site reaction $A \rightarrow B$, the total energy of the system is described by Eq. (1). The formation of the AC changes the local energy of the system by a value equal to a change in the energy of the cluster Hamiltonian

$$\delta h_f^A(K_1) = \sum_{k=1}^z \sum_{j_k=1}^s [v_f^{A*}(K_1) - v_f^A(K_1) - \delta \varepsilon_{fg_k}^{A_{jk}}(K_1)] \gamma_f^A \Gamma_{\{g\}}^{(j)}(K_1), \quad (26)$$

where

$$\delta \varepsilon_{fg_k}^{A_{jk}}(K_1) = \varepsilon_{fg_k}^{*A_{jk}}(K_1) - \varepsilon_{fg_k}^{A_{jk}}(K_1).$$

The probability of AC reaction $A \rightarrow B$ occurring at site f of reaction cluster K_1 is that of a complex event: particle A occurring at site f upon a change in the system's energy by the value of $\delta h_f^A(K_1)$. It is expressed as

$$W(\{\gamma_f^A\} \rightarrow \{\gamma_f^B\}) = \gamma_f^A U_f^A(K_1), \quad (27)$$

$$U_f^A(K_1) = \exp[-\beta \delta h_f^A(K_1)].$$

The exponential dependence in (27) is due to the assumption that AC has chemical potential μ_A^* and is in equilibrium with a reaction subsystem consisting of initial reagent A and the fixed arrangement of all neighboring particles around A , interaction with which determines the activation barrier height. We are talking here about the local equilibrium (reagent–AC), though the distribution of particles over lattice sites and the equilibrium distribution can differ as much as possible. As shown above (see the text between formulas (1) and (2)), the chemical potential is associated with internal motions of AC in $v_f^{A*}(K_1)$ through AC statistical sum $Q_f^{*A}(K_1)$. By distinguishing the translational degree of freedom along the reaction coordinate from the AC statistical sum and expressing the rate of the motion along it using characteristics of the activation barrier $U_f^A = \kappa \omega \theta_f^{*A}(K_1) / \delta$, where all values have their usual meaning [6, 33, 45–47] (κ is the transmission coefficient; ω is the average rate of the AC's motion along the vertex of the activation barrier with length δ ; $\theta_f^{*A}(K_1)$ is the concentration of AC at the given stage), we obtain an expression for the rate of an elementary process at one site of the system with correlators of the first type (3):

$$U_f^A = \langle \gamma_f^A U_f^A(K_1) \rangle = \sum_{(g_1) \dots (g_j)_z} K_{fg_1 \dots g_z}^{A_{j_1 \dots j_z}} \theta_{fg_1 \dots g_z}^{A_{j_1 \dots j_z}} \exp[\beta \delta \varepsilon_{fg_k}^{A_{jk}}(K_1)], \quad (28)$$

where index k at neighboring site g_k is associated with the same rearrangement of correlators into a sum over

different occupancy states of all neighbors, as in expressions (8) and (9). The rate constant of elementary stages at a fixed distribution of neighbors K_1 , which determines the local activation energy through the energies of the AC and the initial reagent (h is the Planck constant) was introduced in (28):

$$K_{fg_1 \dots g_z}^{A_{j_1 \dots j_z}} = \frac{\kappa Q_f^{*A}(K_1)}{Q_f^A(K_1) h \beta} \exp[\beta (\mu_f^{*A} - \mu_f^A)]. \quad (29)$$

In the right side of (29) there is a difference between the chemical potentials of the AC and the initial reagent to reflect within the LGM the occurrence of a particle from the gas phase not contained in the LGM components. If the AC is formed by components of the lattice system, $\mu_f^{*A} = \mu_f^A$ and Eq. (29) have a common meaning:

$K_{fg_1 \dots g_z}^{A_{j_1 \dots j_z}} = \kappa Q_f^{*A}(K_1) / Q_f^A(K_1) h \beta$. If a gas molecule participates in the formation of the AC (e.g., vacancy V and gas molecule A participate at the stage of adsorption), $\mu_f^{*V} = \mu_f^V + \mu_A$, where μ_A is the chemical potential of molecules A in the gas phase, $\mu_f^{*V} - \mu_f^V = \mu_A$, and its partial pressure appears in formula (29) [6, 19, 25]: $K_{fg_1 \dots g_z}^{A_{j_1 \dots j_z}} = \kappa Q_f^{*A}(K_1) P_A / Q_A h \beta$.

The multi-particle nature of statistical sums $Q_f^{*A}(K_1)$ and $Q_f^A(K_1)$ in (29) does not allow us to transform Eq. (28) into the traditional rate constant of the elementary stage in the form $U_f^A = K_f^A V_f^A$, where K_f^A is the rate constant of the one-site stage in an ideal system and V_f^A is the concentration component of the rate that considers a change in the activation energy because of the non-ideality of the reaction system (as for the pair potential [6, 25, 33]), though $V_f^A = \theta_f^A$ when there is no interaction. With a weak dependence, however, the ratios of statistical sums in (29) from local configurations in the reaction cluster (as when considering indirect correlations at the potential of pair interaction), the structure of (29) allows us to move to the form $U_f^A = K_f^A V_f^A$ in (28).

For a binary system of expressions (28) and (29) and using (n, σ) to determine the configurations, the rates of the stages are written through correlators of the first type, as above:

$$U_f^A = \sum_{n=0}^z \sum_{\sigma(n)} b_{\sigma(n)}^{\sigma(0)} K_f^A(n, \sigma) \theta_f^A([n, \sigma]) \exp[\beta \delta \varepsilon_{fg}^{ij}([n, \sigma])], \quad (30)$$

$$K_f^A(n, \sigma) = \frac{\kappa Q_f^{*A}(n, \sigma)}{Q_f^A(n, \sigma) h \beta} \exp[\beta (\mu_f^{*A} - \mu_f^A)].$$

Parameters of interaction on a homogeneous lattice do not depend on the site numbers and can be character-

ized by the number of particles A in the coordination sphere and their configurations $\sigma(n)$.

In the right side of kinetic equations for all correlators $n > 1$, summands of one-site stages of the $U_{fg}^{(i)j}(\alpha)$ (15) type for $n = 2$ or $I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}$ (1) for any $n > 2$ (25) appear in addition to summands $U_f^i(\alpha)$. The meaning of these summands is that neighboring particle j at site g is in the immediate environment of reacting particle i , and it changes the activation barrier height for the reaction of particle i . The particle itself does not participate in the reaction, and the occupancy state of site g does not change. Summands $U_{fg}^{(i)j}(\alpha)$ are in expression $I_{f_1 f_2 \dots f_n}^{i_1 i_2 \dots i_n}$ (1) for one-site stages that can occur in all n sites of a correlator of this dimensionality. All neighboring sites that are nearest to the reagent and which retain their occupancy states can contain particles affecting the activation barrier height. In these situations, Eq. (28) for the rates retains the correlator dimensionality of n , but a contribution from energy appears in (28), depending on the approximation used to consider correlations between interacting particles:

$$U_{fg}^{(A)j} = \langle \gamma_f^A \gamma_g^j U_f^A(K_1) \rangle \\ = \sum_{(gj)_1 \dots (gj)_z} \text{prime} K_{fg_1 \dots g_z}^{A j_1 \dots j_z} \theta_{fg_1 \dots g_z}^{A j_1 \dots j_z} \exp[\beta \delta \epsilon_{fg_k}^{A j_k}(K_1)], \quad (28a)$$

where the prime mark before the sum over all states of occupancy of sites $g_1 \dots g_z$ means that averaging is not performed over one of the neighboring g sites. Particle j makes a constant contribution to the rate constant through $\exp[\beta \delta \epsilon_{fg_k}^{A j_k}(K_1)]$. For example [6], we introduce Eq. (28a) for the pair potential in the QCA when $n = 2$, $s = 2$, $U_{fg}^{(A)A}$ have the form $U_{fg}^{(A)A} = U_f^A \Psi_{fg}^{AA}$, $\Psi_{fg}^{jA} = t_{hg}^{AA} \exp(\beta \delta \epsilon_{fg}^{AA}) / S_{fg}^A$, where $S_{fg}^A = \sum_j t_{hg}^{AA} \exp(\beta \delta \epsilon_{fg}^{AA})$, $t_{fg}^{AA} = \theta_{fg}^{AA} / \theta_f^A q$, $\delta \epsilon_{fg}^{AA} = \epsilon_{fg}^{*AA} - \epsilon_{fg}^{AA}$, where ϵ_{fg}^{*AA} is the parameter of pair interaction between the AC and initial neighbors. With LGM multi-particle parameters, Eq. (28a) depends on the approximation that is used and correlator dimensionality n .

The derived expressions for the elementary one-site reaction rates must have the property of a self-consistent description of the equilibrium state in the kinetics path to equilibrium. Ideal reaction systems always have this property, since the theory is of a one-particle nature. Problems arise when considering interparticle interactions responsible for the non-ideal behavior of real systems.

The essence of self-consistency is that by equalizing the rates of forward and backward reactions, we obtain the same equation for the equilibrium distribution of reaction mixture components, which immediately follows from the derivation of the equation in the equilibrium theory. From a formal viewpoint, this

means that by equalizing the rates of opposite elementary stages containing AC parameters (the AC's internal statistical sum and energies of interaction between molecules of the system and the AC), we obtain an expression that depends only on the molecular parameters of system components, rather than these AC parameters.

To prove this property, let us consider one-site stage $A \leftrightarrow B$ and write Eq. (4) for correlators of the first type with all indices and central components A and B in the form

$$\theta_{fg_1 \dots g_z}^{A j_1 \dots j_z} \exp \beta \left[v_f^A(K_1) - \sum_{k=1}^z \sum_{j_k=1}^s \epsilon_{fg_k}^{A j_k}(K_1) \right] \\ = \theta_{fg_1 \dots g_z}^{B j_1 \dots j_z} \exp \beta \left[v_f^B(K_1) - \sum_{k=1}^z \sum_{j_k=1}^s \epsilon_{fg_k}^{B j_k}(K_1) \right]. \quad (31)$$

Note that AC properties at the top of the barrier do not depend on the direction of the reaction (i.e., the statistical sum and the AC parameters of potential interaction formed from reagents A and B are the same:

$v_f^{*A}(K_1) = v_f^{*B}(K_1)$ and $\epsilon_{fg_k}^{*A j_k}(K_1) = \epsilon_{fg_k}^{*B j_k}(K_1)$. Let us divide Eq. (31) on the left and right, respectively, by the same value of the exponent with indices $v_f^{*A}(K_1) - \sum_{k=1}^z \sum_{j_k=1}^s \epsilon_{fg_k}^{*A j_k}(K_1)$ and $v_f^{*B}(K_1) - \sum_{k=1}^z \sum_{j_k=1}^s \epsilon_{fg_k}^{*B j_k}(K_1)$. On each side we then have an expression for the local rate of a one-site stage for a fixed configuration of neighbors K_1

$$\theta_{fg_1 \dots g_z}^{A j_1 \dots j_z} \exp \beta \left[v_f^A(K_1) - v_f^{*A}(K_1) + \sum_{k=1}^z \sum_{j_k=1}^s \delta \epsilon_{fg_k}^{A j_k}(K_1) \right] \\ = \theta_{fg_1 \dots g_z}^{B j_1 \dots j_z} \exp \beta \left[v_f^B(K_1) - v_f^{*B}(K_1) + \sum_{k=1}^z \sum_{j_k=1}^s \delta \epsilon_{fg_k}^{B j_k}(K_1) \right]. \quad (32)$$

After the identical averaging of Eq. (32) on the right and on the left over all configurations of neighbors $\{j\}$ on cluster $K_1 = (gj)_1 \dots (gj)_z$, it can be rewritten in the form of (28) with regard to (29). Otherwise we obtain the equality of rates of stage $A \leftrightarrow B$ in opposite directions $U_f^A = U_f^B$.

RATES OF TWO-SITE STAGES

Let us consider two-site stages of the form $A + C \rightarrow B + D$ at two central sites f and h [6, 25, 33, 35]. The AC of the two-site stage occupies two sites f and h . Neighbors of reaction cluster K_2 are all neighbors g located at the shortest distance from one of the sites of the central pair of sites f and h with reagents $A + C$. Dimensionality K_2 is $2(z-1) + 2 = 2z$, if neighboring $(z-1)$ sites for central sites f and h do not intersect. If they do intersect, dimensionality K_2 is less than $2z$. (For a 2D lattice where $z = 6$, dimensionality K_2 is $2(z-1)$.) To simplify denotation, below we consider

dimensionality K_2 to be $2z$ for all lattice structures and refer to the total number of sites of the nearest neighbors g as $2z$ ($1 \leq g \leq 2z$), though it can be smaller (e.g., $2(z-1)$).

In analogy with above denotaion $\Gamma_{\{g\}}^{(j)}(K_1)$ for one-site clusters K_1 , we accept $\Gamma_{\{g\}}^{(j)}(K_2) = \gamma_{g_1}^{j_1} \dots \gamma_{g_{2z}}^{j_{2z}}$ for the states of all neighbors of cluster K_2 and introduce a system of correlators of the first type, constructed at two central sites f and h :

$$\begin{aligned} \theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} &= \langle \gamma_f^A \gamma_h^C \Gamma_{\{g\}}^{(j)}(K_2) \rangle = \langle \gamma_f^A \gamma_h^C \gamma_{g_1}^{j_1} \dots \gamma_{g_{2z}}^{j_{2z}} \rangle \\ &= \frac{\text{const}(j_1 \dots j_{2z})}{Q} \\ &\times \exp \beta \left[-v_{fh}^{AC}(K_2) + \sum_{k=1}^{2z} \sum_{j_k=1}^s \varepsilon_{fhg_k}^{ACj_k}(K_2) \right]. \end{aligned} \quad (33)$$

The meaning of all values introduced is similar to that of the above parameters for one-site clusters K_1 with initial Hamiltonian (1). For simplicity, we retain the form of the denotation of LGM multi-particle parameters that describe internal motions $v_{fh}^{AC}(K_2) = v_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}}$ and interparticle interactions $\varepsilon_{fhg_k}^{ACj_k}(K_2) = \varepsilon_{fhg_k\{g_1 \dots g_{2z}\}}^{ACj_k\{j_1 \dots j_{2z}\}}$. Neighboring sites g , $1 \leq g \leq 2z$, are located asymmetrically around f and h , and two distances are required between neighbor g and two central sites f and h [6, 25, 33]. One index k , $1 \leq k \leq 2z$, is used to simplify the denotations in (33). Here, $v_{fh}^{AC}(K_2) = v_f^A(K_1) + v_h^C(K_1) - \tilde{\varepsilon}_{fh}^{AC}(K_2)$, where the last summand means that energy $\tilde{\varepsilon}_{fh}^{AC}(K_2)$ of bond fh is considered twice in both $v_f^A(K_1)$ and $v_h^C(K_1)$. The value of $\tilde{\varepsilon}_{fh}^{AC}(K_2)$ corresponds to bond fh , so it depends on the model of multi-particle interactions. The simplest version of symmetrization is $\tilde{\varepsilon}_{fh}^{AC}(K_2) = \frac{1}{2}(\tilde{\varepsilon}_{fh}^{AC}(K_1) + \tilde{\varepsilon}_{hf}^{CA}(K_1))$, which is an approximation of the quantum chemical calculations of bonds in [26, 27].

The ratio of correlators of the first type and different pairs of central sites allows us to exclude the unknown constant and statistical sum of system Q , yielding an expression with a structure similar to that of Eq. (4) for clusters K_1 :

$$\begin{aligned} \theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} / \theta_{fhg_1 \dots g_{2z}}^{BDj_1 \dots j_{2z}} &= \exp \beta \left[v_{fh}^{BD}(K_2) - v_{fh}^{AC}(K_2) \right. \\ &\left. + \sum_{k=1}^{2z} \sum_{j_k=1}^s [\varepsilon_{fhg_k}^{ACj_k}(K_2) - \varepsilon_{fhg_k}^{BDj_k}(K_2)] \right] = M_{fhg_1 \dots g_{2z}}^{ACBD\{j\}}. \end{aligned} \quad (34)$$

Correlators of the second type are defined as

$$\theta_{fhg_1 \dots g_n}^{ACj_1 \dots j_n} = \langle \gamma_f^A \gamma_h^C \gamma_{g_1}^{j_1} \dots \gamma_{g_n}^{j_n} \rangle, \quad 0 \leq n \leq 2z. \quad (35)$$

The relationship between the correlators of the first and second types retains the structure of (6)

$$\theta_{fhg_1 \dots g_n}^{ACj_1 \dots j_n} = \langle \gamma_f^A \gamma_h^C \gamma_{g_1}^{j_1} \dots \gamma_{g_n}^{j_n} \rangle = \sum_{j_{n+1}} \dots \sum_{j_{2z}} \theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}}. \quad (36)$$

As above, correlators of the second type for two central sites of different dimensionalities are associated with one another by normalization conditions (12), which are satisfied for any characteristic time scale τ .

In the transitional state, AC interacts with neighboring particles, with parameter of interaction

$$\varepsilon_{fhg_k}^{*ACj_k}(K_2) = \varepsilon_{fhg_k\{g_1 \dots g_{2z}\}}^{*ACj_k\{j_1 \dots j_{2z}\}} \quad \text{differing from}$$

$\varepsilon_{fhg_k}^{ACj_k}(K_2) = \varepsilon_{fhg_k\{g_1 \dots g_{2z}\}}^{ACj_k\{j_1 \dots j_{2z}\}}$ between initial reagent i , from which AC is formed, and neighboring particle j . The total energy of the system is also described by Eq. (1) when there is no AC of one-site reaction $A \rightarrow B$. The formation of the AC changes the local energy of the system, and it becomes equal to a change in the cluster Hamiltonian by the value

$$\begin{aligned} \delta h_{fh}^{AC}(K_2) &= \sum_{k=1}^{2z} \sum_{j_k=1}^s [v_{fh}^{*AC}(K_2) - v_{fh}^{AC}(K_2) \\ &- \delta \varepsilon_{fhg_k}^{ACj_k}(K_2)] \gamma_f^A \gamma_h^C \Gamma_{\{g\}}^{(j)}(K_2), \end{aligned} \quad (37)$$

where $\delta \varepsilon_{fhg_k}^{ACj_k}(K_2) = \varepsilon_{fhg_k}^{*ACj_k}(K_2) - \varepsilon_{fhg_k}^{ACj_k}(K_2)$.

The probability of the formation of the AC of reaction $A + C \rightarrow B + D$ at site f of reaction cluster K_2 is that of a complex event: particle A being at site f , particle C being at site h , and a change in the system's energy by the value of $\delta h_{fh}^{AC}(K_2)$. It is expressed as

$$\begin{aligned} W(\{\gamma_f^A \gamma_h^C\} \rightarrow \{\gamma_f^B \gamma_h^D\}) &= \gamma_f^A \gamma_h^C U_{fh}^{AC}(K_2), \\ U_{fh}^{AC}(K_2) &= \exp[-\beta \delta h_{fh}^{AC}(K_2)]. \end{aligned} \quad (38)$$

As in (27), the exponential dependence in (38) and the use of the concept of the chemical potential μ_A^* are associated with the assumption that the AC is in equilibrium with a reaction subsystem consisting of initial reagents A and C and the fixed arrangement of all neighboring particles $\{j\}$ around AC $A + C$, interaction with which determines the activation barrier height. As above, we assume local equilibrium (reagent-AC), though the distribution of particles over the lattice sites can differ from the equilibrium distribution as much as possible.

According to [6, 33, 35], two-site stage rate $U_{fh}^{AC} = \langle \gamma_f^A \gamma_h^C U_{fh}^{AC}(K_2) \rangle$ is expressed through the total set of correlators of the first type and dimensionality K_2 . By distinguishing between the translational degree of freedom along the reaction coordinate and the AC statistical sum, we obtain $Q_{fh}^{*AC}(K_2)$ and repeat the same as for the AC of the one-site reaction. By expressing the rate of motion along it through barrier

to activation characteristics $U_{fh}^{*AC} = \kappa\omega\theta_{fh}^{*AC}(K_2)/\delta$, where all values have a common meaning, and $\theta_{fh}^{*AC}(K_2)$ is the concentration of the AC of the considered two-site stage, we obtain an expression for the elementary rate of the process through correlators of the first type per system site:

$$U_{fh}^{AC} = \langle \gamma_f^A \gamma_h^C U_{fh}^{AC}(K_2) \rangle = \sum_{(g\bar{f})_1 \dots (g\bar{f})_{2z}} K_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} \theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} \times \exp[\beta(-\tilde{\epsilon}_{fh}^{AC}(K_2) + \delta\epsilon_{fhg_k}^{ACj_k}(K_2))], \quad (39)$$

where the $\tilde{\epsilon}_{fh}^{AC}(K_2)$ value that appears when the local contribution from the AC is considered is the energy of reagents A and C before their transformation into the AC (the fh bonding energy is internal for the AC and is not written in explicit form. As above, the symbol of index k at neighboring site g_k in the exponent is due to the rearrangement of correlators into the sum over different occupancy states of all neighbors. Here, the rate constant of an elementary stage is also introduced at the fixed distribution of neighbors K_2 defining the local activation energy through the energies of the AC and initial reagents (where h is the Planck constant):

$$K_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} = \frac{\kappa Q_{fh}^{*AC}(K_2)}{Q_f^A(K_1)Q_h^C(K_1)h\beta} \times \exp[\beta(\mu_{fh}^{*AC} - \mu_f^A - \mu_h^C)]. \quad (40)$$

As in (29), the difference of chemical potentials of AC and the initial reagent is introduced into the right side of (40) to reflect within the LGM the presence of a particle from the gas phase that is not one of its components. If the AC is formed from lattice system components, $\mu_{fh}^{*AC} = \mu_f^A + \mu_h^C$ and Eq. (40) have a common

meaning: $K_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} = \kappa Q_{fh}^{*AC}(K_2)/[Q_f^A(K_1)Q_h^C(K_1)h\beta]$. If a gas molecule participates in the formation of the AC (e.g., two neighboring vacancies V and gas molecule A_2 participate in the stage of dissociative adsorption, $\mu_{fh}^{*VV} = \mu_f^V + \mu_h^V + \mu_{A_2}$, where μ_{A_2} is the chemical potential of molecules A_2 in the gas phase), then $\mu_{fh}^{*VV} - \mu_f^V - \mu_h^V = \mu_{A_2}$, $\mu_f^{*V} - \mu_f^V = \mu_{A_2}$, and partial pressure P_{A_2} appears in formula (40) [6, 25, 27]: $K_{fhg_1 \dots g_{2z}}^{VVj_1 \dots j_{2z}} = \kappa Q_{fh}^{*VV}(K_2)P_{A_2}/[Q_{A_2}h\beta]$.

In the right sides of kinetic equations for all correlators $n > 1$, summands appear for two-site stages of type $U_{fgh}^{(ij)b}(\alpha)$ (15) when $n = 2$ and $P_{f_1f_2 \dots f_n}^{i_1i_2 \dots i_n}$ for when $n > 2$ (25), in addition to $U_{fgh}^{ij}(\alpha)$. As above, particle j in the immediate environment of reacting particle i does not participate in the reaction, but its presence changes the activation barrier height for the reaction of parti-

cle i . In these situations, Eq. (39) for the rates raises the correlator's dimensionality by one ($n + 1$) from each new neighbor, and an energy contribution appears in (39) that depends on the approximation used to consider correlations between interacting particles

$$U_{fhg}^{(AC)j} = \langle \gamma_f^A \gamma_h^C \gamma_g^j U_{fh}^{AC}(K_2) \rangle = \sum_{(g\bar{f})_1 \dots (g\bar{f})_{2z}} \text{' } K_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} \theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} \times \exp[\beta(-\tilde{\epsilon}_{fh}^{AC}(K_2) + \delta\epsilon_{fhg_k}^{ACj_k}(K_2))], \quad (39a)$$

where the prime mark before the sum over all occupancy states of sites $g_1 \dots g_{2z}$ in (39a) means that averaging does not include one of neighboring sites g , $1 \leq g \leq 2z$. Particle j makes a constant contribution to the rate constant (40) through $\exp[\beta\delta\epsilon_{fhg_k}^{ACj_k}(K_2)]$. For example [6], let us consider Eq. (39a) for the pair potential in QCA at $n = 2$, $s = 2$. Function $U_{fhg}^{(VA)A}$ has the form $U_{fhg}^{(VA)A} = U_{hf}^{VA} \Psi_{fg}^{AA}$, $\Psi_{fg}^{AA} = t_{hg}^{AA} \exp(\beta\delta\epsilon_{fg}^{AA})/S_{fg}^A$, where all values are defined above. With LGM multi-particle parameters, Eq. (39a) depends on the approximation that is used and correlator dimensionality n .

For correlators with two central sites we can prove the self-consistency of the description of forward and backward stage rates and local equilibrium. Let us consider two-site stage $A + C \leftrightarrow B + D$, and for central components ($A + C$) and ($B + D$) we write an expression for correlators of the first type (34) in the equivalent form

$$\theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} \exp \beta \left[v_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} - \sum_{k=1}^{2z} \sum_{j_k=1}^s \delta\epsilon_{fhg_k}^{ACj_k}(K_2) \right] = \theta_{fhg_1 \dots g_{2z}}^{BDj_1 \dots j_{2z}} \exp \beta \left[v_{fhg_1 \dots g_{2z}}^{BDj_1 \dots j_{2z}} - \sum_{k=1}^{2z} \sum_{j_k=1}^s \delta\epsilon_{fhg_k}^{BDj_k}(K_2) \right]. \quad (41)$$

Note that AC properties at the top of the barrier do not depend on the reaction direction (i.e., statistical sums and potential interaction parameters of the AC formed from reagents A and B are the same: $v_{fh}^{*AC}(K_2) = v_{fh}^{*BD}(K_2)$ and $\epsilon_{fhg_k}^{*ACj_k}(K_2) = \epsilon_{fhg_k}^{*BDj_k}(K_2)$). We divide equality (41) on the left and right, respectively, by the same value of the exponent with indices $v_{fh}^{*AC}(K_2) - \sum_{k=1}^{2z} \sum_{j_k=1}^s \epsilon_{fhg_k}^{*ACj_k}(K_2)$ and $v_{fh}^{*BD}(K_2) - \sum_{k=1}^{2z} \sum_{j_k=1}^s \epsilon_{fhg_k}^{*BDj_k}(K_2)$. On each side we then have an expression for the local one-site stage rate at a fixed configuration of neighbors K_2 :

$$\begin{aligned}
 & \theta_{fhg_1 \dots g_{2z}}^{ACj_1 \dots j_{2z}} \exp \beta \left[v_{fh}^{AC}(K_2) - v_{fh}^{*AC}(K_2) \right. \\
 & \quad \left. + \sum_{k=1}^{2z} \sum_{j_k=1}^s (\varepsilon_{fhg_k}^{*ACj_k}(K_2) - \varepsilon_{fhg_k}^{ACj_k}(K_2)) \right] \\
 & = \theta_{fhg_1 \dots g_{2z}}^{BDj_1 \dots j_{2z}} \exp \beta \left[v_{fh}^{BD}(K_2) - v_{fh}^{*BD}(K_2) \right. \\
 & \quad \left. + \sum_{k=1}^{2z} \sum_{j_k=1}^s (\varepsilon_{fhg_k}^{*BDj_k}(K_2) - \varepsilon_{fhg_k}^{BDj_k}(K_2)) \right].
 \end{aligned} \quad (42)$$

Equation (42) corresponds to reaction cluster K_2 as a whole, and we have neither the isolation of contributions from clusters K_1 nor the values of $\tilde{\varepsilon}_{fh}^{AC}(K_2)$ and $\tilde{\varepsilon}_{fh}^{BD}(K_2)$. By doing the same averaging over all configurations of neighbors $\{j\}$ on cluster $K_2 = (gj)_1 \dots (gj)_{2z}$ on the right and left sides of Eq. (42), we can rewrite (42) in the form of (39). Otherwise, we obtain the equality of rates of stage $A + C \leftrightarrow B + D$ in opposite directions: $U_{fh}^{AC} = U_{fh}^{BD}$.

In this section, we do not present an analog of Eq. (9) for correlators of the second type with two central sites for multi-particle potentials because it is cumbersome. In [35], we gave an example of applying this equation and deriving functions of indirect correlations for dissociative adsorption for the potential of pair interaction. We also proved the compatibility of equilibrium systems of equations for correlators of the second type constructed at one and two central sites.

CLOSURE OF KINETIC EQUATIONS AND RATES OF ELEMENTARY STAGES

The derived structure of the system of kinetic equations for correlators from unary ($n = 1$) to size n contains contributions U_f^A (28) from reaction correlators of dimensionalities K_1 and K_2 on the right for one-site stages and U_{fh}^{AC} (39) with correlators K_2 and larger due to two-site stages. To close a system of kinetic equations we must express $U_f^A = U_f^A(\theta_i, \theta_{ij}, \theta_{ijk} \dots)$ and $U_{fh}^{AC} = U_{fh}^{AC}(\theta_i, \theta_{ij}, \theta_{ijk} \dots)$, where $\theta_i, \theta_{ij}, \theta_{ijk} \dots$ is the set of independent correlators of the second type that describe molecular distributions for the selected level of the accuracy of approximation. This set of correlators is identical for contributions (28) and (39).

The dimensionality of reaction correlators K_1 and K_2 always exceeds that of unknown coupled correlators n on the left, and these equations are derived for their evolution. Kinetic equations for unary (concentrations) and pair DFs are usually considered. For the potential of pair interaction, the QCA corresponds to adequate closure of the reaction correlators [6, 25].

The occurrence of multi-particle effects renders the QCA unsatisfactory, and a more accurate description of the system's evolution is required.

The following principle must be met when dealing with multi-particle correlators in statistical physics [3–6, 25–44]: If the right sides of a system of equilibrium or non-equilibrium equations contain correlators of a higher order than those in the left side, we must derive new equations that describe their equilibrium or kinetic states. This means that multi-particle LGM parameters in the model of associates requires the use of calculations that allow consideration of k order correlations that are not lower than order n of multi-particle molecular LGM parameters. Otherwise, inconsistency is possible when describing thermodynamic functions (TFs) by different means. It is therefore essential to manage the use of the CF approach with dimensionalities $k < n$ and substantiate the correctness of their application [1]. This means that a general rule for such a closure in kinetics must be equality $k = n$.

The derived equations for multi-particle LGM parameters in compliance with this principle show that the following dimensionalities of coupled correlators through which stage rates must be expressed are possible: either the sequence of correlators, starting from triple to size k ; or correlator K_1 for one-site stages; or correlator K_2 and higher if there are two-site stages. When considering the anharmonism of intermolecular vibrations for nearest neighbors in bound associates, order n therefore reaches a value of at least $(1 + z)$ in all phases. For volume $d = 3, z = 12$ this gives the minimum correlator dimensionality of 13, which surpasses the traditional magnitudes of k and n substantially.

The need to solve kinetic equations with correlators that have high dimensionalities dramatically complicates solving the problem. We must employ reduced kinetic equations using the condition of local equilibrium, with allowance for different time intervals in relaxation for reagents and solvent molecules.

In non-ideal reaction systems, we must identify equilibrium states in which mixture components manage to mix quickly in space and react (the entire system is in equilibrium), or the components are quickly mixed but not all of them manage to react, and there is no complete chemical equilibrium in the system (processes are described by equations for concentrations $d\theta_i/d\tau$). The second case is typical of chemical kinetics: all components are distributed in equilibrium in the system volume, and correlators in expressions for the rates of elementary stages obey equilibrium distribution equations (9).

Equalities $d\theta_{ij}/d\tau = 0$ in (15), which signify equilibrium in pair functions, correspond to the local equilibrium condition. Recalling that in Bogolyubov's hierarchy of times [41], the temporal dependence of

pair DF for a multicomponent mixture is written as $\theta_{fg}^{ij}(x_f^i, x_g^j, \tau) = \theta_{fg}^{ij}(x_f^i, x_g^j, \tau, \theta_f^i(x_f^i, \tau), \theta_g^j(x_g^j, \tau))$, where x_f^i denotes the position of particle i in the full phase space of the system. (Here, symbol x_f^i is a coordinate in LGM.) The choice of independent variables in full pair CFs corresponds to the structure of the time hierarchy between CFs of different dimensionalities. Independent variables for time dependences are non-equilibrium unary functions $\theta_f^i(x_f^i, \tau)$ and $\theta_g^j(x_g^j, \tau)$ that describe a synchronous contribution to the evolution of pair CFs, and the explicit dependence of pair a CF itself $\theta_{fg}^{ij}(x_f^i, x_g^j, \tau)$ is the relaxation contribution to the evolution of pair CF. It is the temporal dependence of relaxation contribution $\partial\theta_{fg}^{ij}(x_f^i, x_g^j, \tau)/\partial\tau$ (15) that determines the local equilibrium condition: $\partial\theta_{fg}^{ij}(x_f^i, x_g^j, \tau)/\partial\tau \rightarrow 0$ must be met [48].

The above refers to the equilibrium distribution of components to a very important class of conditions for the practical calculation of kinetic processes. To calculate the equilibrium distribution of components with more accurate consideration of correlation effects than that of the QCA, we must employ the current means of statistical physics [49–51]: matrix, fragment, cluster variational, and stochastic numerical means. (We do not discuss here problems of their practical application.)

Apart from the above approaches to approximately describing systems with multi-particle effects, it was proposed in [1] that less accurate systems of equations be used, but only if the possibility the correctly describing TFs was retained. Let us recall the kinetic equations in [41–44] and in this work were derived for CFs in the LGM using the CA. Molecular distributions from the CA and other equations of statistical physics obtained using the CF approach are not directly related to calculating free energy F or the statistical sum of system Q ($F = -k_B T \ln(Q)$), so the problem arises of how to calculate free energy F by means of molecular distributions in the CA.

It was proposed in [1] that model free energy F_{mod} be introduced, provided it was constructed so as to satisfy both the equilibrium and non-equilibrium conditions of the system. This was because the expressions for the potential contribution of internal energy $U_{\text{mod}}^{\text{pot}}$ and entropy S_{mod} with correlators do not depend on the degree of equilibrium of the system state. Kinetic contribution $U_{\text{mod}}^{\text{kin}}$ of the internal energy must therefore satisfy the principle of the self-consistent description of system states that can be considered in the CF approach, but not in that of statistical sums. The expression for F_{mod} is then identical in both the equilibrium and non-equilibrium states, and its use provides a more general approach to describing a system's properties. The expression for F_{mod} is written formally

as $F_{\text{mod}} = U_{\text{mod}} - TS_{\text{mod}}$, where U_{mod} is the model free energy and S_{mod} is the model entropy. $U_{\text{mod}} = U_{\text{mod}}^{\text{pot}} + U_{\text{mod}}^{\text{kin}}$ consists of potential and kinetic contributions. Summand $U_{\text{mod}}^{\text{pot}}$ denotes all forms of potential functions (including multi-particle contributions), and summand $U_{\text{mod}}^{\text{kin}}$ is constructed on the basis of the CA, ensuring the above condition of self-consistency.

As shown above, the expressions in the CA for correlators are derived through the relationship with the chemical potential found from the system of equilibrium equations $\mu_i(\theta_i, \theta_{ij}, \theta_{ijk} \dots)$, where $\theta_i, \theta_{ij}, \theta_{ijk} \dots$ is the same set of independent correlators describing molecular distributions for the selected level of the accuracy of approximation, as in expressions (28) and (39). On the other hand, $\mu_i = -\partial F_{\text{mod}}(\{\theta_f^i, \theta_{fg}^{ij}, \dots\})/\partial N_i|_{V,T}$, which allows us to associate calculations of the free energy and chemical potentials. Here, pressure $P = -\partial F_{\text{mod}}(\{\theta_f^i, \theta_{fg}^{ij}, \dots\})/\partial V_{N,T}$ can be used under conditions close to equilibrium, since equations for the correlators are described by kinetic equations that become equations for equilibrium if the stage rates that are used correspond to the principle of self-consistency.

CONCLUSIONS

Multi-particle energy parameters $\varepsilon_{fgk}^{ijk}(K_1) = \varepsilon_{fgk}^{ijk\{j_1 \dots j_z\}}_{fgk\{g_1 \dots g_z\}}$ were introduced as additives to pair potentials in the model of associates [1]. Multi-particle parameters can generally be introduced into the LGM, depending on the aim of the analysis and the nature of the given system, since multi-particle energy parameters are introduced clearly [52–54]. We can use coordinate description $\varepsilon_{fg}^{ij}(K_1) = \varepsilon_{fg_1 \dots g_z}^{ij_1 \dots j_z}$ of the energy of associates or clusters that might be introduced as a result of calculations using quantum chemical means [26, 27] without specifying pair potentials. These distinctions alter the description of the energy contributions slightly, but the main feature of CA is still the rates of elementary stages being expressed through correlators of the first type with respective multi-particle energy contributions when the states of initial reagents change as they transition to the activated state within the theory of absolute reaction rates of non-ideal systems. (Note that this way of deriving kinetic equations and the rates of elementary stages fully corresponds to replacing the equilibrium process of reaching the top of the activation barrier with a dynamic level-by-level description of a change in the energy of reagents [55, 56].)

New equations for the pair interaction potential between a system's components allow refinement of the QCA (with its direct correlations) by allowing for

indirect correlations. The theory is literally generalized for considering interactions of the second and next neighbors.

This way of deriving kinetic equations permits generalization from a rigid lattice structure to a soft (deformed) lattice structure [1, 48]. This allows correct calculations of pressure with regard to its experimentally measured periods of relaxation with respect to that of the chemical potential. The concept of F_{mod} allows us to consider coupled correlators of any dimensionalities from $n = 2, 3, \dots$ to K_1 and further. The use of F_{mod} combines the introduced model representations of multi-particle internal motions in the LGM [1] in both rigid and soft lattices.

The ideas of the cluster approach do not depend on the type of the potential or the statistical sum of internal motions of system components. They operate with a full set of system configurations and can be applied to its non-equilibrium states. The self-consistent equations for the equilibrium and non-equilibrium spatial molecular distributions derived in the LGM with regard to the potential of multi-particle interaction and the dependence of internal molecular motions on the configurations of neighboring molecules (and their composition and structure in bound associates [1]) greatly expand the possibilities of calculating the kinetics of physicochemical processes. These equations can be applied not only to vapor–liquid phases (as in [1]) but to all heterogeneous three-aggregate systems as well, including adsorption systems with contributions from the anharmonism of molecular vibrations [20–24, 57–60].

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CONFLICT OF INTEREST

The author declares he has no conflicts of interest.

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