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Time-Dependent Statistics of Binary Linear Lattices

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The time-dependent statistics of binary linear lattices is investigated on the basis of a master equation at the microscopic level. It is assumed that the kinetics may be formulated as transformations of specified sequences of clusters of A units and B units into other specified sequences. On the basis of a *Stosszahlansatz*, a master equation at the macroscopic level is derived. In the limit of a large system, the densities of clusters of all types satisfy rate equations similar to the equations of chemical kinetics. An H-theorem is proven and the nonequilibrium thermodynamics of the system is studied. The theory has application to the kinetics of the helix-coil phase transition in biopolymers.

KEY WORDS: Nonequilibrium statistics; polymers; helix-coil transition; chemical kinetics; Ising chain.

1. INTRODUCTION

The study of the kinetics of binary linear lattices has application to a range of physical systems The systems under consideration may be represented schematically by a linear array of N units, each of which can be in either of two states, A or B. A nonequilibrium state of the system is described by a probability distribution $p(\mathrm{s}, t)$ on the set of configurations $\mathrm{s} \equiv (s_1, s_2, \ldots, s_N)$, where the variables s_j take the values A or B. It is assumed that the microscopic kinetics of the system is known and that the time dependence

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of the probability distribution is governed by a master equation

$$\partial p(\mathrm{s}, t)/\partial t = \sum_{\mathrm{s}'} [w(\mathrm{s}, \mathrm{s}')\, p(\mathrm{s}', t) - w(\mathrm{s}', \mathrm{s})\, p(\mathrm{s}, t)] \tag{1}$$

where $w(\mathrm{s}', \mathrm{s})$ is the transition probability per unit time for the transition from the configuration s to s′. Both internal stochastic interactions between units and interactions with an external agency or heat bath can give rise to the transitions. In each physical situation, the magnitudes of the transition probabilities must be found from a more detailed microscopic theory. It is the purpose of this paper to develop methods for the approximate solution of the master equation (1).

Approximate methods are desired because Eq. (1) can rarely be solved explicitly, an exact solution being feasible only for some special choices of the transition probabilities.(1–5) The $w(\mathrm{s}', \mathrm{s})$ are characterized partly by the time-independent equilibrium solution of (1). Briefly, exact solutions are limited to the case where the equilibrium is that of the Ising chain with nearest-neighbor interactions in the absence of a magnetic field, or without interactions in the presence of a magnetic field. The approximate method of solution developed in the present article applies to a wide class of systems characterized by equilibrium statistics in which clusters of neighboring A units or B units are statistically independent. The Ising chain is included in this class as a special case.

Our work was inspired mainly by its possible application to the theory of the kinetics of phase transitions, in particular the helix-coil transition in biopolymers. An elaborate and lucid discussion of the equilibrium statistics is given in the monograph by Poland and Scheraga,(6) where extensive references to related work may be found. Some additional features of equilibrium which bear relevance to the present work were elucidated in a previous article,(7) to be referred to as I. Alternative approaches to the time-dependent problem with specific reference to the helix-coil transition were proposed previously in the work by Gō,(8) Schwarz,(9) Craig and Crothers,(10) and Silberberg and Simha.(11)

Our approximation method is based on a contracted description in terms of the occupation numbers of the different types of clusters. In Section 2, a master equation for the probability distribution of these variables is derived on the basis of a plausible *Stosszahlansatz*. Since the occupation numbers are extensive variables proportional to the total number of units N, the formal parameter expansion of van Kampen(12) may be applied. The transition probabilities $w(\mathrm{s}', \mathrm{s})$ are formulated in terms of reactions of sequences of neighboring clusters. It is shown in subsequent sections that the macroscopic equations for the densities of clusters of all types are very similar to the rate equations of chemical kinetics. It should be stressed that these equations are rigorously valid in the limit $N \to \infty$ once the coarse-grained master equation is assumed. The general features of the macroscopic rate equations are discussed in analogy with the theory of chemical kinetics.(13) An H-theorem is derived and its relation to the nonequilibrium thermodynamics of the system is studied. In the final section, we briefly discuss possible extensions and applications of our work.

2. STOSSZAHLANSATZ AND COARSE-GRAINED MASTER EQUATION

As mentioned in the introduction, our analysis is based on a description of the system in terms of occupation numbers of A clusters and B clusters. In order to make this more explicit, we note that each configuration s is also completely specified by a linear sequence of A_l and B_m clusters, e.g.,

$$A_{l_1}, B_{m_1}, A_{l_2}, B_{m_2}, \ldots, A_{l_n} \tag{2}$$

Let n_{A_l} be the number of A_l clusters in the configuration s, and n_{B_m} the number of B_m clusters. We shall abbreviate $n_l \equiv n_{A_l}$ and $n_m \equiv n_{B_m}$. A state x of the system is defined by the set of occupation numbers $\mathrm{x} = \{n_l, n_m\}$. We define

$$\begin{aligned} N_A &= \sum_{l=1}^{\infty} l n_l, \qquad N_B = \sum_{m=1}^{\infty} m n_m \\ M_A &= \sum_{l=1}^{\infty} n_l, \qquad M_B = \sum_{m=1}^{\infty} n_m \end{aligned} \tag{3}$$

Note that $N_A + N_B = N$ and that M_A and M_B can differ at most by unity. The total number of configurations s giving rise to the same set of occupation numbers x is

$$\Omega(\mathrm{x}) = [M_A(\mathrm{x})!/\textstyle\prod_l n_l!][M_B(\mathrm{x})!/\prod_m n_m!](1 + \delta_{M_A, M_B}) \tag{4}$$

Sometimes, it is convenient to specify the nature of the end clusters explicity, e.g., $\Omega^{if}(\mathrm{x})$, where i and f take the values A or B and indicate the nature of the first and last clusters. The number $\Omega^{if}(\mathrm{x})$ is given by (4) with omission of the last factor.

We assume that the thermal equilibrium situation has the properties described in I, i.e., in equilibrium clusters are statistically independent with weight factors

$$u_l = \exp[-\epsilon_l/k_B T], \qquad v_m = \exp[-\epsilon_m/k_B T] \tag{5}$$

where k_B is Boltzmann's constant and T absolute temperature, so that the total weight of the state **x** is

$$G(\mathbf{x}) = \prod_{l,m} u_l^{n_l} v_m^{n_m} \tag{6}$$

For simplicity, we neglect that the end clusters frequently have different statistical weights. In equilibrium, the statistical weights of all configurations **s** corresponding to the same state x are equal. The equilibrium probability distribution is

$$p_{\text{eq}}(\mathrm{s}) = P_{\text{eq}}[\mathrm{x(s)}]/\Omega[\mathrm{x(s)}] \tag{7}$$

with

$$P_{\text{eq}}(\mathrm{x}) = \Omega(\mathrm{x})G(\mathrm{x})/Z_N \tag{8}$$

where Z_N is the canonical partition function.

We assume that the transition probabilities $w(\mathrm{s}', \mathrm{s})$ may be classified in terms of reactions of sets of neighboring clusters. For example, an important reaction will be

$$A_l + B_m + A_{l'} \rightarrow A_{l+m+l'} \tag{9}$$

where by definition the clusters named on the left-hand side must occur as neighbors, in the order written, somewhere in the configuration s, and s' differs from s only in the replacement of the clusters $(A_l B_m A_{l'})$ by $A_{l+m+l'}$. The most general reaction of this type is

$$r: \qquad C_{k_1} + C_{k_2} + \cdots + C_{k_n} \rightarrow C_{k_1'} + C_{k_2'} + \cdots + C_{k_p'} \tag{10}$$

where C_k indicates either an A_l or a B_m cluster. Of course, A and B clusters must alternate in both the initial and final complexes. The reaction (10) will be written for short

$$r: \qquad \{C\}_r \rightarrow \{C'\}_r \tag{11}$$

where $\{C\}_r$ is the ordered set of reactants and $\{C'\}_r$ the ordered set of reaction products. Apart from the ordering, a reaction is characterized completely by a set of stoichiometric coefficients $\{\nu_{l,r}, \nu_{m,r}\}$. The coefficient $\nu_{l,r}$ (or $\nu_{m,r}$) equals the number of times the cluster A_l (or B_m) occurs on the right side of the reaction equation minus the number of times it occurs on the left side. The stoichiometric coefficients satisfy the following constraints:

$$\begin{gathered} \sum_l \nu_{l,r} = \sum_m \nu_{m,r} \\ \sum_l l\nu_{l,r} + \sum_m m\nu_{m,r} = 0 \end{gathered} \tag{12}$$

The first constraint implies that the total number of (dis)appearing A clusters must equal the total number of (dis)appearing B clusters. The second constraint implies that the total number of units N is conserved in reactions. In most physical applications, only simple reactions involving a small number of reactants and reaction products will be of any importance.

Our statistical analysis is based on the following *Stosszahlansatz*: If at some initial time t, the probability distribution $p(\mathbf{s}, t)$ is uniform over the set of configurations $\mathbf{s}$ corresponding to the state $\mathbf{x}$ and if this is true for all states $\mathbf{x}$, then to a good approximation, uniformity is preserved in the course of time.

The *Stosszahlansatz* implies that the original master equation (1) which is valid on a microscopic level may be replaced by a master equation valid on a more macroscopic level. Define the probability distribution $P(\mathbf{x}, t)$ by

$$P(\mathbf{x}, t) = \sum_{\mathbf{s}} p(\mathbf{s}, t)\, \delta[\mathbf{x}(\mathbf{s}) - \mathbf{x}] \tag{13}$$

If $p(\mathbf{s}, t)$ is uniform over $\mathbf{s} \in \mathbf{x}$, one has

$$P(\mathbf{x}, t) = p(\mathbf{s}, t)\Omega(\mathbf{x}) \tag{14}$$

Summing (1) over $\mathbf{s} \in \mathbf{x}$ and assuming uniformity, one derives the following master equation for $P(\mathbf{x}, t)$:

$$\partial P(\mathbf{x}, t)/\partial t = \sum_{\mathbf{x}'} [W(\mathbf{x}, \mathbf{x}')\, P(\mathbf{x}', t) - W(\mathbf{x}', \mathbf{x})\, P(\mathbf{x}, t)] \tag{15}$$

where the transition probabilities $W(\mathbf{x}', \mathbf{x})$ are found from $w(\mathbf{s}', \mathbf{s})$ by averaging over the initial configurations $\mathbf{s} \in \mathbf{x}$ and summing over the final configurations $\mathbf{s}' \in \mathbf{x}'$,

$$W(\mathbf{x}', \mathbf{x}) = \sum_{\mathbf{s}, \mathbf{s}'} w(\mathbf{s}', \mathbf{s})\, \delta[\mathbf{x}(\mathbf{s}') - \mathbf{x}']\, \delta[\mathbf{x}(\mathbf{s}) - \mathbf{x}]/\Omega(\mathbf{x}) \tag{16}$$

According to the *Stosszahlansatz*, the master equation (15) is valid at all times.

As usual in the derivation of master equations on a macroscopic level, it is difficult to assess the range of validity of Eq. (15). Presumably, this range is wider the larger the total number of units N and the simpler the reaction kinetics implied in the transition probabilities $w(\mathbf{s}', \mathbf{s})$. We hope to investigate the validity of Eq. (15) in more detail for cases where the original master equation (1) may be solved exactly.

The same coarse-graining employed in the derivation of (15) may be applied to the calculation of averages of observables $f(\mathbf{s})$. The time-dependent average is

$$\begin{aligned}\langle f(\mathbf{s})\rangle_t &= \sum_{\mathbf{s}} f(\mathbf{s})\, p(\mathbf{s}, t)\\ &\approx \sum_{\mathbf{x}} F(\mathbf{x})\, P(\mathbf{x}, t)\end{aligned} \tag{17}$$

where $F(\mathbf{x})$ is the smoothed observable

$$F(\mathbf{x}) = \sum_{\mathbf{s}} f(\mathbf{s})\, \delta[\mathbf{x}(\mathbf{s}) - \mathbf{x}]/\Omega(\mathbf{x}) \tag{18}$$

Of course, when $f(\mathbf{s})$ is uniform over $\mathbf{s} \in \mathbf{x}$, the second equality in (17) is exact. We shall, in fact, deal exclusively with observables of this type.

3. CALCULATION OF TRANSITION PROBABILITIES

In this section, we shall evaluate the transition probabilities $W(\mathbf{x}', \mathbf{x})$ from the microscopic transition probabilities $w(\mathbf{s}', \mathbf{s})$ using Eq. (16). It is convenient to make explicit the occurrence of a reaction r of the type (11) in the transition $\mathbf{s} \to \mathbf{s}'$ by the notation $w_r(\mathbf{s}', \mathbf{s})$. The microscopic transition probability may be written

$$w_r(\mathbf{s}', \mathbf{s}) = \omega_r\, \delta_r(\mathbf{s}', \mathbf{s}) \tag{19}$$

where ω_r is the elementary rate constant for the reaction r and where $\delta_r(\mathbf{s}', \mathbf{s})$ is unity if $\mathbf{s}$ and $\mathbf{s}'$ differ by the occurrence of the reaction r and is zero otherwise. Let $\varphi_r(\mathbf{s}) \equiv n(\{C\}_r\,;\mathbf{s})$ be the number of times the initial complex $\{C\}_r$ occurs in the configuration $\mathbf{s}$. Then, the number of possible reactions r taking the state $\mathbf{x}$ to $\mathbf{x}'$ is given by

$$\begin{aligned}&\sum_{\mathbf{s}',\mathbf{s}} \delta_r(\mathbf{s}', \mathbf{s})\, \delta[\mathbf{x}(\mathbf{s}') - \mathbf{x}']\, \delta[\mathbf{x}(\mathbf{s}) - \mathbf{x}]\\ &\quad = \delta(\mathbf{x} - \mathbf{x}' + \boldsymbol{\nu}_r) \sum_{\mathbf{s}} \varphi_r(\mathbf{s})\, \delta[\mathbf{x}(\mathbf{s}) - \mathbf{x}]\end{aligned} \tag{20}$$

where the stoichiometric vector $\boldsymbol{\nu}_r$ is a shorthand notation for the set of stoichiometric coefficients $\{\nu_{l,r}, \nu_{m,r}\}$. Hence one finds, using (16),

$$W_r(\mathbf{x}', \mathbf{x}) = \omega_r \Phi_r(\mathbf{x})\, \delta(\mathbf{x} - \mathbf{x}' + \boldsymbol{\nu}_r) \tag{21}$$

where $\Phi_r(\mathbf{x})$ is the average number of possibilities for the reaction r to start from the state $\mathbf{x}$,

$$\Phi_r(\mathbf{x}) = \sum_{\mathbf{s}} \varphi_r(\mathbf{s})\, \delta[\mathbf{x}(\mathbf{s}) - \mathbf{x}]/\Omega(\mathbf{x}) \tag{22}$$

or, in case we restrict the average to configurations with specified end conditions,

$$\Phi_r(\mathbf{x}; if) = \langle n(\{C\}_r)\rangle_{\mathbf{x}}^{if} \tag{23}$$

In the average (23), all configurations $\mathbf{s} \in \mathbf{x}$ with end conditions (i, f) receive equal weight $1/\Omega^{if}(\mathbf{x})$.

We introduce the notation

$$\boldsymbol{\nu}_r = \boldsymbol{\gamma}_r' - \boldsymbol{\gamma}_r \tag{24}$$

where $\boldsymbol{\gamma}_r \equiv \{\gamma_{l,r}, \gamma_{m,r}\}$ counts the reactants in the reaction r and $\boldsymbol{\gamma}_r' \equiv \{\gamma_{l,r}', \gamma_{m,r}'\}$ counts the reaction products. By definition, all components of $\boldsymbol{\gamma}_r$ and $\boldsymbol{\gamma}_r'$ are nonnegative. Let α denote whether the last cluster before the initial complex $\{C\}_r$ consists of A's or B's and let β be the corresponding indicator for the first cluster following $\{C\}_r$. Then, the average (23) may be written

$$\langle n(\{C\}_r)\rangle_{\mathbf{x}}^{if} = \sum_{\mathbf{x}', \mathbf{x}''} \Omega^{i\alpha}(\mathbf{x}')\, \Omega^{\beta f}(\mathbf{x}'')\, \delta(\mathbf{x}' + \mathbf{x}'' + \boldsymbol{\gamma}_r - \mathbf{x})/\Omega^{if}(\mathbf{x}) \tag{25}$$

since the complex $\{C\}_r$ must occur somewhere in the chain, if at all, and when its position is specified, we must count the number of configurations consistent with $\mathbf{x}$. Hence we may also write

$$\langle n(\{C\}_r)\rangle_{\mathbf{x}}^{if} = [M_A(\mathbf{x}) - m_A(\{C\}_r) + 1 - \delta_{iA}\delta_{\alpha A} - \delta_{fA}\delta_{\beta A}]\, \Omega'(\mathbf{x} - \boldsymbol{\gamma}_r)/\Omega^{if}(\mathbf{x}) \tag{26}$$

where $m_A(\{C\}_r)$ is the number of A clusters in $\{C\}_r$ and where $\Omega'(\mathbf{x} - \boldsymbol{\gamma}_r)$ is defined by (4) with omission of the last factor. The first factor in (26) is just the total number of possible positions of the complex $\{C\}_r$ on the chain of clusters with specified end conditions. The second factor then counts the remaining degeneracy. As an example, we evaluate the average (26) for some simple initial complexes, namely $\{C\}_r = A_l B_m$ and $\{C\}_r = A_l B_m A_{l'}$,

$$\begin{aligned} \langle n(A_l B_m)\rangle_{\mathbf{x}}^{if} &= \{(M_A - \delta_{fA})/[M_A + \delta_{if}(\delta_{fA} - \delta_{fB})]\}\, n_l n_m/M_A \\ \langle n(A_l B_m A_{l'})\rangle_{\mathbf{x}}^{if} &= n_l n_m (n_{l'} - \delta_{ll'})/M_A M_B \end{aligned} \tag{27}$$

Thus, using (21), (23), and (26), one finds an explicit expression for the transition probability $W_r(\mathbf{x}', \mathbf{x})$ in terms of the occupation numbers and the elementary rate constant ω_r.

4. DETAILED BALANCE

In most applications, reactions occur in pairs of forward and backward reactions, e.g.,

$$\begin{aligned} a: &\quad \{C\}_a \rightarrow \{C'\}_a \\ b: &\quad \{C'\}_a \rightarrow \{C\}_a \end{aligned} \tag{28}$$

Obviously,

$$\{C\}_b = \{C'\}_a\,, \qquad \{C'\}_b = \{C\}_a \tag{29}$$

An arbitrary convention may decide whether a reaction is forward or backward. We assume that for all reaction pairs, a detailed balance relation holds between the forward and backward rate constants $\omega_a \equiv \omega(\{C'\}_a|\{C\}_a)$ and $\omega_b \equiv \omega(\{C\}_a|\{C'\}_a)$ of the form

$$\omega(\{C'\}_a\,|\{C\}_a) \prod_{l,m} u_l^{\gamma_{l,a}} v_m^{\gamma_{m,a}} = \omega(\{C\}_a\,|\{C'\}_a) \prod_{l,m} u_l^{\gamma'_{l,a}} v_m^{\gamma'_{m,a}} \tag{30}$$

This is equivalent to a detailed balance relation between the transition probabilities $W_a(\mathbf{x}', \mathbf{x})$ and $W_b(\mathbf{x}', \mathbf{x})$, namely

$$W_a(\mathbf{x}', \mathbf{x})P_{\text{eq}}(\mathbf{x}) = W_b(\mathbf{x}, \mathbf{x}')P_{\text{eq}}(\mathbf{x}') \tag{31}$$

In order to show the equivalence, we derive (30) from (31). Using (21), one finds from (31)

$$\omega_a \Phi_a(\mathbf{x})P_{\text{eq}}(\mathbf{x}) = \omega_b \Phi_b(\mathbf{x} + \boldsymbol{\nu}_a)P_{\text{eq}}(\mathbf{x} + \boldsymbol{\nu}_a) \tag{32}$$

Inserting the explicit expression (8) for the equilibrium distribution and the expression (26) for the average frequency of occurrence of initial reaction complexes, one easily deduces (30) from (32) when use is made of the obvious relation

$$M_A(\mathbf{x}') - m_A(\{C'\}_a) = M_A(\mathbf{x}) - m_A(\{C\}_a) \tag{33}$$

and the fact that the nature of the end clusters in the sequences $\{C\}_a$ and $\{C'\}_a$ must be the same.

If all reactions are paired in the above manner, one derives a detailed balance relation for the total transition probabilities,

$$W(\mathbf{x}', \mathbf{x})P_{\text{eq}}(\mathbf{x}) = W(\mathbf{x}, \mathbf{x}')P_{\text{eq}}(\mathbf{x}') \tag{34}$$

by summing (31) over all forward and backward reactions. Equation (34) is sufficient to ensure that any initial distribution $P(\mathbf{x}, t)$ tends to a limiting distribution proportional to $P_{\mathrm{eq}}(\mathbf{x})$ within every subset of states $\mathbf{x}$ mutually connected by nonvanishing transition probabilities. If all states $\mathbf{x}$ are mutually connected, $P(\mathbf{x}, t)$ tends to $P_{\mathrm{eq}}(\mathbf{x})$ as t tends to infinity.

5. RATE EQUATIONS

From the master equation (15), one easily derives equations for the moments of the probability distribution $P(\mathbf{x}, t)$. For our purposes, only the first two moments are of interest. They are defined by

$$\begin{aligned} \langle \mathbf{x} \rangle_t &= \sum_{\mathbf{x}} \mathbf{x} P(\mathbf{x}, t) \\ \langle \Delta\mathbf{x}\, \Delta\mathbf{x} \rangle_t &= \sum_{\mathbf{x}} \Delta\mathbf{x}\, \Delta\mathbf{x}\, P(\mathbf{x}, t) \end{aligned} \tag{35}$$

where

$$\Delta\mathbf{x} = \mathbf{x} - \langle \mathbf{x} \rangle_t . \tag{36}$$

From (15), one finds, using (21),

$$\begin{aligned} (\partial/\partial t)\langle \mathbf{x} \rangle_t &= \sum_r \omega_r \boldsymbol{\nu}_r \langle \Phi_r(\mathbf{x}) \rangle_t \\ (\partial/\partial t)\langle \Delta\mathbf{x}\, \Delta\mathbf{x} \rangle_t &= \sum_r \omega_r [\boldsymbol{\nu}_r \langle \Delta\mathbf{x}\, \Phi_r(\mathbf{x}) \rangle_t + \langle \Delta\mathbf{x}\, \Phi_r(\mathbf{x}) \rangle_t \boldsymbol{\nu}_r + \boldsymbol{\nu}_r \boldsymbol{\nu}_r \langle \Phi_r(\mathbf{x}) \rangle_t] \end{aligned} \tag{37}$$

Evidently, the rate of change of the first two moments is determined by higher moments of the distribution. This leads generally to a hierarchy of coupled moment equations the solution of which is as difficult as the original master equation (15).

At this point, we make use of the redeeming feature that one is usually interested in the behavior of large systems. In the limit $N \to \infty$, exact equations may be derived for the first two moments. Essentially, this is a consequence of the central limit theorem, which states that under general conditions, probability distributions of sum variables become Gaussian in the limit of a large number of variables. In our case, the variables are the configurations $\mathbf{s}$ and the sum variables are the states $\mathbf{x}$. For the explicit formal derivation, one may use van Kampen's parameter expansion of the master equation(12) and reduce the equation to a Fokker–Planck equation. In the present case, the large parameter is the total number of units N. Higher-order corrections may be obtained by systematic expansion. In this paper, we shall deal exclusively with the macroscopic rate equations for the first moments $\langle \mathbf{x} \rangle_t$ and leave the study of fluctuations to future work. In I, we have already studied fluctuations in equilibrium.

Van Kampen's work is based on the observation that for probability distributions of interest, one has in the limit of large N,

$$\langle \mathbf{x} \rangle_t = N\boldsymbol{\rho}(t) + O(N^{1/2}) \tag{38}$$

where $\boldsymbol{\rho}(t) \equiv \{\rho_l(t), \rho_m(t)\}$ are the densities of A clusters and B clusters on the chain. Similarly, one finds, using (26),

$$\langle \Phi_r(\mathbf{x}) \rangle_t = N\rho \prod_{l,m} f_l^{\gamma_{l,r}} f_m^{\gamma_{m,r}} + O(N^{1/2}) \tag{39}$$

where ρ is the total A- or B-cluster density defined by

$$\rho(t) = \lim_{N\to\infty} (1/N)\langle M_A \rangle_t = \sum_l \rho_l(t) = \sum_m \rho_m(t) \tag{40}$$

The cluster probabilities f_l and f_m are defined by

$$f_k = \rho_k/\rho, \qquad k = l, m \tag{41}$$

Note that (39) is in agreement with the expression (I.4.8) derived for thermal equilibrium. From (37)–(39), one finds in the limit $N \to \infty$, the macroscopic rate equations

$$\partial\boldsymbol{\rho}/\partial t = \rho \sum_r \boldsymbol{\nu}_r J_r \tag{42}$$

where the reaction rates J_r are given by

$$J_r = \omega_r \prod_{l,m} f_l^{\gamma_{l,r}} f_m^{\gamma_{m,r}} \tag{43}$$

Summing (42) over the components l or m, one finds that the total cluster density varies according to

$$\partial\rho/\partial t = -\Gamma(t)\rho(t) \tag{44}$$

where the total coagulation rate $\Gamma(t)$ is given by

$$\Gamma(t) = \sum_r J_r \Delta_r\,, \qquad \Delta_r = -\sum_l \nu_{l,r} = -\sum_m \nu_{m,r} \tag{45}$$

Using (44), one may write (42) alternatively as an equation for the cluster probabilities f_k,

$$(\partial\mathbf{f}/\partial t) - \Gamma\mathbf{f} = \sum_r \boldsymbol{\nu}_r J_r \tag{46}$$

This is a closed set of equations of the same type as the rate equations for a reacting mixture of chemical species. From the solution of (46) one may calculate the coagulation rate $\Gamma(t)$, and hence from (44), the cluster density $\rho(t)$, for given initial conditions at time $t = 0$.

A macroscopic quantity of independent interest is the average A fraction. In the limit $N \to \infty$, it is defined by

$$\theta(t) = \sum_l l\rho_l(t) \tag{47}$$

From (42), one finds that its rate of change is given by

$$(\partial/\partial t)\,\theta(t) = -\rho \sum_r J_r \Lambda_r \tag{48}$$

where

$$\Lambda_r = -\sum_l l\nu_{l,r} = \sum_m m\nu_{m,r} \tag{49}$$

Again, the complete solution of the rate equations (46) is needed for the evaluation of $\theta(t)$.

6. DETAILED BALANCE AND *H*-THEOREM

We specialize to the case that all reactions occur in pairs of forward and backward reactions. The rate equations (46) may then be written

$$(\partial \mathbf{f}/\partial t) - \Gamma \mathbf{f} = \sum_a \boldsymbol{\nu}_a (J_a - J_b) \tag{50}$$

and the coagulation rate Γ is

$$\Gamma = \sum_a (J_a - J_b)\,\Delta_a \tag{51}$$

where we have used

$$\boldsymbol{\nu}_a = -\boldsymbol{\nu}_b \tag{52}$$

The detailed balance relation (30) may be cast in the form

$$\omega_a \prod_{l,m} (f_l^{eq})^{\gamma_{l,a}} (f_m^{eq})^{\gamma_{m,a}} = \omega_b \prod_{l,m} (f_l^{eq})^{\gamma'_{l,a}} (f_m^{eq})^{\gamma'_{m,a}} \tag{53}$$

where we have used the relation (I.4.1)

$$f_l^{eq} = {z_0}^l u_l / U(z_0), \qquad f_m^{eq} = {z_0}^m v_m / V(z_0) \tag{54}$$

Here, z_0 is related to the equilibrium free energy per unit φ_{eq} by

$$\varphi_{\mathrm{eq}} = k_B T \ln z_0 \tag{55}$$

and the denominators are normalizing factors. The smallest root of the condition

$$U(z_0)V(z_0) = 1 \tag{56}$$

determines the magnitude of z_0. Using (56) and the constraints (12), one easily shows that (30) and (53) are equivalent. From (43), it follows that the detailed balance relation may also be written

$$J_a^{eq} = J_b^{eq} \tag{57}$$

Hence in equilibrium, $\Gamma^{\mathrm{eq}} = 0$ and $\partial\, \mathbf{f}^{\mathrm{eq}}/\partial t = 0$.

The detailed balance relation permits us to derive an important inequality which is of use in proving an H-theorem. We define nonequilibrium chemical potentials by

$$\mu_k = k\varphi_{eq} + k_B T \ln(f_k/f_k^{eq}), \qquad k = l, m \tag{58}$$

and corresponding affinities

$$\begin{aligned} \mathcal{A}_r &= -\sum_l \nu_{l,r}\mu_l - \sum_m \nu_{m,r}\mu_m \\ &= -k_B T \sum_l \nu_{l,r} \ln(f_l/f_i^{eq}) - k_B T \sum_m \nu_{m,r} \ln(f_m/f_m^{eq}) \end{aligned} \tag{59}$$

Evidently, the affinities vanish in equilibrium. For each pair of forward and backward reactions a and b, one has

$$\mathcal{A}_a = -\mathcal{A}_b \tag{60}$$

and the affinity $\mathcal{A}_a$ may also be written

$$\mathcal{A}_a/k_B T = \ln(J_a/J_a^{eq}) - \ln(J_b/J_b^{eq}) \tag{61}$$

where we have used (24) and (43). Hence one finds for each pair of reactions a and b using the detailed balance relation (57)

$$\begin{aligned} &\mathcal{A}_a J_a + \mathcal{A}_b J_b \\ &\quad = k_B T J_a^{eq}[(J_a/J_a^{eq}) - (J_b/J_b^{eq})][\ln(J_a/J_a^{eq}) - \ln(J_b/J_b^{eq})] \geqslant 0 \end{aligned} \tag{62}$$

with the equality sign holding only in equilibrium. If all reactions occur in pairs of forward and backward reactions, one has

$$\sum_r \mathcal{A}_r J_r \geqslant 0 \tag{63}$$

Now, define the H-function

$$H = \rho \left[\sum_l f_l \ln(f_l/f_l^{eq}) + \sum_m f_m \ln(f_m/f_m^{eq})\right] \tag{64}$$

Then, one finds by straightforward calculation from the macroscopic rate equations in the form (44) and (46)

$$dH/dt = -(\rho/k_B T) \sum_r \mathcal{A}_r J_r \leqslant 0 \tag{65}$$

with the equality sign holding only in equilibrium. Hence H decreases monotonically till it reaches its value zero in equilibrium. The function H therefore serves as a Liapounov function and the system of rate equations is asymptotically stable in the sense of Liapounov. For any initial state, the cluster probabilities f_l and f_m and the cluster density ρ eventually attain their equilibrium values as t tends to infinity.

7. NONEQUILIBRIUM THERMODYNAMICS

The H-function introduced in the preceding section is closely related to the nonequilibrium free energy of the chain, as will now be shown. From (4), it follows that in the thermodynamic limit $N \to \infty$, the entropy per unit when the system is in the state x is given by

$$\begin{aligned} s &= \lim_{N\to\infty} (1/N)\, k_B \ln \Omega(\mathbf{x}) \\ &= k_B \left[\left(\sum_l \rho_l\right) \ln \left(\sum_l \rho_l\right) - \sum_l \rho_l \ln \rho_l \right. \\ &\quad \left. + \left(\sum_m \rho_m\right) \ln \left(\sum_m \rho_m\right) - \sum_m \rho_m \ln \rho_m\right] \end{aligned} \tag{66}$$

The energy per unit is

$$\begin{aligned} e &= \lim_{N\to\infty} (1/N)\left(\sum_l n_l \epsilon_l + \sum n_m \epsilon_m\right) \\ &= \sum_l \rho_l \epsilon_l + \sum_m \rho_m \epsilon_m \end{aligned} \tag{67}$$

where ϵ_l is the energy of an A_l cluster and ϵ_m the energy of a B_m cluster. As has been discussed in I, these energies incorporate both internal cluster energies and interactions with neighbors. The nonequilibrium free energy per unit is given by

$$\varphi = e - Ts \tag{68}$$

The free energy may be regarded as a functional $\varphi(\rho)$ of the cluster densities ρ_l and ρ_m. We recall that the cluster densities satisfy the constraints

$$\sum_l \rho_l = \sum_m \rho_m \tag{69a}$$

$$\sum_l l\rho_l + \sum_m m\rho_m = 1 \tag{69b}$$

The first constraint is a consequence of the fact that A and B clusters alternate on the chain, and the second arises from the expression of the total number of units in terms of the cluster densities.

Minimizing $\varphi(\rho)$ with respect to the cluster densities ρ_l and ρ_m subject to the constraints (69), one finds the conditions

$$\begin{aligned} \epsilon_l + k_BT \ln(\rho^{eq}/\rho_l^{eq}) + \psi - l\mu_0 &= 0 \\ \epsilon_m + k_BT \ln(\rho^{eq}/\rho_m^{eq}) - \psi - m\mu_0 &= 0 \end{aligned} \tag{70}$$

where ψ is the Lagrange parameter corresponding to the constraint (69a) and μ_0 the Lagrange parameter corresponding to (69b). Hence one recovers the expressions (54) for the equilibrium cluster probabilities

$$\begin{aligned} f_l^{eq} &= z_0^l[\exp(-\epsilon_l/k_BT)]/U(z_0) \\ f_m^{eq} &= z_0^m[\exp(-\epsilon_m/k_BT)]/V(z_0) \end{aligned} \tag{71}$$

with the interpretation

$$\begin{aligned} \mu_0 &= \varphi_{\mathrm{eq}} = k_BT \ln z_0 \\ \psi &= -k_BT \ln U(z_0) = k_BT \ln V(z_0) \end{aligned} \tag{72}$$

The entropy per unit (66) may also be written

$$s = -k_B\rho \left[\sum_l f_l \ln f_l + \sum_m f_m \ln f_m\right] \tag{73}$$

Using (69) and (71), one finally finds that the H-function and the nonequilibrium free energy are related by

$$\varphi = \varphi_{\mathrm{eq}} + k_BTH \tag{74}$$

From the H-theorem (65) derived in the previous section, it follows that the free energy per unit φ decreases monotonically to its equilibrium value φ_{eq}.

Finally, we note from (58) and (69b) that the free energy may be expressed in terms of the chemical potentials by

$$\varphi = \sum_l \rho_l \mu_l + \sum_m \rho_m \mu_m \tag{75}$$

so that φ may be interpreted as the Gibbs free energy.

8. EXAMPLES OF SOME SIMPLE REACTIONS

As an illustration of the theory developed in the preceding sections, we treat some examples of reaction equations which, because of their simplicity, will be of importance in physical applications. As a first example, we consider A growth by p units. A typical member of the set of forward reactions is

$$a(l, m): \qquad A_l + B_m \rightarrow A_{l+p} + B_{m-p} \tag{76}$$

The corresponding backward equation is

$$b(l, m): \qquad A_{l+p} + B_{m-p} \rightarrow A_l + B_m \tag{77}$$

The stoichiometric coefficients are

$$\nu_{l',a} = -\delta_{l',l} + \delta_{l',l+p}\,, \qquad \nu_{m',a} = -\delta_{m',m} + \delta_{m',m-p} \tag{78}$$

Hence

$$\Delta_a = 0, \qquad \Lambda_a = -p \tag{79}$$

so that the coagulation rate Γ vanishes identically. The reaction rates are

$$J_{a(l,m)} = \omega_{a(l,m)} f_l f_m\,, \qquad J_{b(l,m)} = \omega_{b(l,m)} f_{l+p} f_{m-p} \tag{80}$$

where the rate constants read more explicity

$$\begin{aligned} \omega_{a(l,m)} &= \omega(A_{l+p}B_{m-p} | A_l B_m) \equiv \omega_+(l, m) \\ \omega_{b(l,m)} &= \omega(A_l B_m | A_{l+p} B_{m-p}) \equiv \omega_-(l + p, m - p) \end{aligned} \tag{81}$$

The detailed balance relation (30) reads

$$\omega_+(l, m) u_l v_m = \omega_-(l + p, m - p) u_{l+p} v_{m-p} \tag{82}$$

The rate equations (46) are

$$\begin{aligned}\partial f_l/\partial t &= \sum_m f_m[\omega_+(l-p, m)f_{l-p} + \omega_-(l+p, m)f_{l+p} - \omega_+(l, m)f_l - \omega_-(l, m)f_l]\\ \partial f_m/\partial t &= \sum_l f_l[\omega_+(l, m+p)f_{m+p} + \omega_-(l, m-p)f_{m-p} - \omega_+(l, m)f_m - \omega_-(l, m)f_m]\end{aligned} \tag{83}$$

The rate of change of the A-fraction θ is, from (48),

$$\partial\theta/\partial t = \rho p \sum_{l,m} [\omega_+(l, m) - \omega_-(l, m)]f_l f_m \tag{84}$$

Of course, if several growth reactions occur for different values of p, the equations (83) and (84) must be summed over p. Finally, the affinity for the reaction $a(l, m)$ is

$$\mathcal{A}_+(l, m) = \mu_l + \mu_m - \mu_{l+p} - \mu_{m-p} \tag{85}$$

As a second example, we consider the class of A-coagulation reactions

$$a(l, m, l'), b(l, m, l'): \qquad A_l + B_m + A_{l'} \rightleftarrows A_{l+m+l'} \tag{86}$$

The stoichiometric coefficients are

$$\nu_{l'',a} = -\delta_{l'',l} - \delta_{l'',l'} + \delta_{l'',l+m+l'}, \qquad \nu_{m',a} = -\delta_{m',m} \tag{87}$$

Hence

$$\Delta_a = 1, \qquad \Lambda_{a(l,m,l')} = -m \tag{88}$$

The reaction rates are

$$J_{a(l,m,l')} = \omega_{a(l,m,l')}f_l f_m f_{l'}, \qquad J_{b(l,m,l')} = \omega_{b(l,m,l')}f_{l+m+l'} \tag{89}$$

with rate constants

$$\begin{aligned}\omega_{a(l,m,l')} &\doteq \omega(A_{l+m+l'}|A_l B_m A_{l'}) \equiv \omega(l+m+l'|l, m, l')\\ \omega_{b(l,m,l')} &= \omega(A_l B_m A_{l'}|A_{l+m+l'}) \equiv \omega(l, m, l'|l+m+l')\end{aligned} \tag{90}$$

which satisfy the detailed balance relation

$$\omega(l+m+l'|l, m, l')u_l v_m u_{l'} = \omega(l, m, l'|l+m+l')u_{l+m+l'} \tag{91}$$

The rate equations read

$$
\begin{aligned}
(\partial f_l/\partial t) - \Gamma f_l & \\
& \sum_{l',m,l''} [\omega(l \mid l', m, l'') f_{l'} f_m f_{l''} - \omega(l', m, l'' \mid l) f_l] \\
& + \sum_{l',m} \{[\omega(l, m, l' \mid l+m+l') + \omega(l', m, l \mid l'+m+l)] f_{l+m+l'} \\
& - [\omega(l+m+l' \mid l, m, l') + \omega(l'+m+l \mid l', m, l)] f_l f_m f_{l'}\} \\
(\partial f_m/\partial t) - \Gamma f_m & \\
& = \sum_{l,l'} [\omega(l, m, l' \mid l+m+l') f_{l+m+l'} - \omega(l+m+l' \mid l, m, l') f_l f_m f_{l'}]
\end{aligned} \tag{92}
$$

The coagulation rate is

$$
\Gamma(t) = \sum_{l,m,l'} [\omega(l+m+l' \mid l, m, l') f_l f_m f_{l'} - \omega(l, m, l' \mid l+m+l') f_{l+m+l'}] \tag{93}
$$

and the rate of change of the A fraction is

$$
\begin{aligned}
\partial\theta/\partial t = \rho \sum_{l,m,l'} m[\omega(l+m+l' \mid l, m, l') f_l f_m f_{l'} \\
- \omega(l, m, l' \mid l+m+l') f_{l+m+l'}]
\end{aligned} \tag{94}
$$

Finally, the affinity for the reaction $a(l, m, l')$ is

$$
\mathcal{A}_{a(l,m,l')} = \mu_l + \mu_m + \mu_{l'} - \mu_{l+m+l'} \tag{95}
$$

The equations for the corresponding process of B-coagulation are easily found by a change of indices.

As mentioned before, in many physical applications, the above processes will be the most important. The explicit values for the rate constants must be found from a detailed microscopic theory or from physical considerations.(14)

9. DISCUSSION

We have studied the time-dependent statistics of a class of binary linear lattices characterized by a thermal equilibrium distribution for which clusters of similar units are statistically independent. Our analysis has proceeded in two steps. On the basis of a *Stosszahlansatz*, we have first replaced the master equation (1) valid on the microscopic level by the master equation (15) for the probability distribution of occupation numbers of clusters. The variables of the latter equation are extensive, and as a second step, we have derived macroscopic rate equations for the densities of cluster species. The latter procedure may be rigorously justified in the limit of large systems. The rate equations are very similar to the equations of chemical kinetics and we have studied their general properties in the framework of nonequilibrium thermodynamics.

The macroscopic rate equations are nonlinear and are therefore difficult to solve analytically. On the other hand, the number of variables involved is enormously smaller than in the original master equation (1), or even (15), and the equations are amenable to numerical solution. At present, a computer study is in progress dealing with the rate equations (83) for $p = 1$ with rate constants corresponding to the helix-coil transition in polypeptides.

The theory is of particular interest for systems showing a phase transition and it opens the possibility of investigating the kinetic processes near the transition point for relatively simple systems, such as polypeptides and polynucleotides. In this regard, it will be worthwhile to extend the theory to a study of fluctuations. In I, we have evaluated the variances of the fluctuations in cluster occupation numbers in thermal equilibrium. As a natural further development of the present theory, we intend to study time correlation functions of equilibrium fluctuations.

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