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A scaling condition for the age of a fluctuation state

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Abstract. The stationary states of age-structured systems are analysed. The condition of stationarity allows us to express the state probabilities in terms of age-averaged transition probabilities. A new scaling hypothesis for the age $a = \tau/V \sim V^{-1}$ (V = the system extension and $\tau \sim V^0$) is suggested which affords the application of Van Kampen and Kubo-Matsuo-Kitahara approximations.

1. Formulation of the problem

Recently, we introduced a new type of age-dependent stochastic process (Vlad *et al* 1984a). Considering a physical system described by a set of macrovariables

$$\boldsymbol{X} = (X_1, \ldots, X_s) \tag{1}$$

and assuming that the transition probabilities

$$W'\Delta t = W(\boldsymbol{X} \to \boldsymbol{X}'; a)\Delta t, \qquad W''\Delta t = W(\boldsymbol{X} \to \boldsymbol{X}''; a)\Delta t, \ldots \tag{2),(3}$$

depend on the age, a, of the state $\boldsymbol{X}$, we proved that the state probability

$$\mathscr{P}\mathrm{d}\boldsymbol{X}\,\mathrm{d}a = \mathscr{P}(\boldsymbol{X}, a; t)\,\mathrm{d}\boldsymbol{X}\,\mathrm{d}a \qquad \int_{\boldsymbol{X}}\int_a \mathscr{P}\,\mathrm{d}\boldsymbol{X}\,\mathrm{d}a = 1, \tag{4}$$

obeys the following system of age-dependent master equations (ADME):

$$\text{ADME:}\begin{cases} (\partial_t + \partial_a)\mathscr{P}(\boldsymbol{X}, a; t) = -\mathscr{P}(\boldsymbol{X}, a; t)\displaystyle\int_{\boldsymbol{X}'} W(\boldsymbol{X} \to \boldsymbol{X}'; a)\,\mathrm{d}\boldsymbol{X}', & (5) \\ \mathscr{P}(\boldsymbol{X}, 0; t) = \displaystyle\int_{\boldsymbol{X}'}\int_{a'} W(\boldsymbol{X}' \to \boldsymbol{X}; a')\mathscr{P}(\boldsymbol{X}', a'; t)\,\mathrm{d}\boldsymbol{X}'\,\mathrm{d}a'. & (6) \end{cases}$$

If

$$W(\boldsymbol{X} \to \boldsymbol{X}'; a) = W(\boldsymbol{X} \to \boldsymbol{X}') = \text{independent of } a, \tag{7}$$

$$W(\boldsymbol{X} \to \boldsymbol{X}''; a) = W(\boldsymbol{X} \to \boldsymbol{X}'') = \text{independent of } a \tag{8}$$

(5) and (6) lead to the well known phenomenological master equation (PME) (Gardiner 1983):

$$\partial_t P(\boldsymbol{X}; t) = \int_{\boldsymbol{X}'} W(\boldsymbol{X}' \to \boldsymbol{X})P(\boldsymbol{X}'; t)\,\mathrm{d}\boldsymbol{X}' - \int_{\boldsymbol{X}'} W(\boldsymbol{X} \to \boldsymbol{X}')P(\boldsymbol{X}; t)\,\mathrm{d}\boldsymbol{X}' \tag{9}$$

where

$$P(\boldsymbol{X};t)=\int_0^\infty \mathcal{P}(\boldsymbol{X},a;t)\,\mathrm{d}a$$

(Vlad *et al* 1984a). Otherwise, the ADME system reduces to a single integral equation in $Z(\boldsymbol{X};t)=\mathcal{P}(\boldsymbol{X},0;t)$ (Vlad *et al* 1984a). In principle, this one may be solved by means of a rather tedious normal mode analysis. For age-dependent transition probabilities, a first attempt to integrate the ADME making use of the Van Kampen (1961, 1976) or Kubo-Matsuo-Kitahara (Kubo *et al* 1973, Kitahara, 1975) approximations failed due to the fact that the corresponding extensivity ansätze are not conserving in time. However, these methods would be applied to steady states provided that a suitable scaling condition of the transition probabilities is to be found. On the other hand, in order to outline the physical meaning of our approach, the analysis of a simple physicochemical system would be of interest. These are the aims of this paper.

2. Steady states

Assuming the existence of a stationary solution

$$\mathcal{P}^{\mathrm{st}}=\mathcal{P}^{\mathrm{st}}(\boldsymbol{X},a) \tag{10}$$

the ADME system becomes

$$\text{ADME:}\begin{cases}\partial_a\mathcal{P}^{\mathrm{st}}(\boldsymbol{X},a)=-\mathcal{P}^{\mathrm{st}}(\boldsymbol{X},a)\displaystyle\int_{\boldsymbol{X}'}W(\boldsymbol{X}\to\boldsymbol{X}';a)\,\mathrm{d}\boldsymbol{X}', & (11)\\ \mathcal{P}^{\mathrm{st}}(\boldsymbol{X},0)=\displaystyle\int_{\boldsymbol{X}'}\int_{a'}W(\boldsymbol{X}'\to\boldsymbol{X};a')\mathcal{P}^{\mathrm{st}}(\boldsymbol{X}',a')\,\mathrm{d}\boldsymbol{X}'\,\mathrm{d}a'. & (12)\end{cases}$$

Equation (11) may be integrated directly giving

$$\mathcal{P}^{\mathrm{st}}(\boldsymbol{X},a)=Z(\boldsymbol{X})\psi(\boldsymbol{X},a), \tag{13}$$

where

$$Z(\boldsymbol{X})=\mathcal{P}^{\mathrm{st}}(\boldsymbol{X},0), \tag{14}$$

$$\psi(\boldsymbol{X},a)=\exp\left(-\int_{\boldsymbol{X}'}\int_{\mu=0}^{a}W(\boldsymbol{X}\to\boldsymbol{X}';\mu)\,\mathrm{d}\boldsymbol{X}'\,\mathrm{d}\mu\right). \tag{15}$$

Introducing the probabilities

$$P^{\mathrm{st}}(\boldsymbol{X})=\int_0^\infty \mathcal{P}^{\mathrm{st}}(\boldsymbol{X},a)\,\mathrm{d}a,\qquad \int_{\boldsymbol{X}}P^{\mathrm{st}}(\boldsymbol{X})\,\mathrm{d}\boldsymbol{X}=1, \tag{16}$$

$$R^{\mathrm{st}}(a|\boldsymbol{X})=\mathcal{P}^{\mathrm{st}}(\boldsymbol{X},a)/P^{\mathrm{st}}(\boldsymbol{X}),\qquad \int_0^\infty R^{\mathrm{st}}(a|\boldsymbol{X})\,\mathrm{d}a=1. \tag{17}$$

Equations (14) and (15) yield

$$P^{\mathrm{st}}(\boldsymbol{X})=Z(\boldsymbol{X})\int_0^\infty \psi(\boldsymbol{X},a)\,\mathrm{d}a, \tag{18}$$

$$R^{\mathrm{st}}(a|\boldsymbol{X})=\psi(\boldsymbol{X},a)\left(\int_0^\infty \psi(\boldsymbol{X},a)\,\mathrm{d}a\right)^{-1}. \tag{19}$$

Combining now (17) and (19) we get

$$\mathscr{P}^{st}(\boldsymbol{X}, a) = P^{st}(\boldsymbol{X})\psi(\boldsymbol{X}, a)\left(\int_0^\infty \psi(\boldsymbol{X}, a)\,\mathrm{d}a\right)^{-1}, \tag{20}$$

where we see that the integration of ADME reduces to the finding out of $P^{st}(\boldsymbol{X})$.

Eliminating $Z(\boldsymbol{X})$ and $\mathscr{P}^{st}(\boldsymbol{X}, a)$ from (12), (14), (18) and (20) leads to a linear homogeneous integral equation for $P^{st}(\boldsymbol{X})$:

$$P^{st}(\boldsymbol{X}) = \int_{\boldsymbol{X}'}\int_{a'=0}^\infty P^{st}(\boldsymbol{X}')\,W(\boldsymbol{X}' \to \boldsymbol{X}; a')\psi(\boldsymbol{X}', a')$$
$$\times\left(\int_0^\infty \psi(\boldsymbol{X}, a)\,\mathrm{d}a\right)\left(\int_0^\infty \psi(\boldsymbol{X}', a)\,\mathrm{d}a\right)^{-1}\mathrm{d}\boldsymbol{X}'\,\mathrm{d}a'. \tag{21}$$

This equation, together with the normalisation condition $\int P^{st}\,\mathrm{d}X = 1$ determines the probability $P^{st}(\boldsymbol{X})$.

A more convenient form of (21) results from integrating (11) over a, yielding

$$\mathscr{P}^{st}(\boldsymbol{X}, \infty) - \mathscr{P}^{st}(\boldsymbol{X}, 0) = -\int_{\boldsymbol{X}'}\int_0^\infty \mathscr{P}^{st}(\boldsymbol{X}, a)\,W(\boldsymbol{X} \to \boldsymbol{X}'; a)\,\mathrm{d}\boldsymbol{X}'\,\mathrm{d}a. \tag{22}$$

As $P^{st}(\boldsymbol{X})$ is finite, from (16) and (18) it follows that

$$\mathscr{P}^{st}(\boldsymbol{X}, \infty) = 0, \qquad \psi(\boldsymbol{X}, \infty) = 0. \tag{23), (24}$$

Eliminating $\mathscr{P}^{st}(\boldsymbol{X}, 0)$ between (12) and (22), inserting $\mathscr{P}^{st}(\boldsymbol{X}, a)$ from (20) and making use of (23) we obtain

$$\int_{\boldsymbol{X}'}[P^{st}(\boldsymbol{X}')\,\tilde{W}(\boldsymbol{X}' \to \boldsymbol{X}) - P^{st}(\boldsymbol{X})\,\tilde{W}(\boldsymbol{X} \to \boldsymbol{X}')]\,\mathrm{d}\boldsymbol{X}' = 0 \tag{25}$$

where

$$\tilde{W}(\boldsymbol{X} \to \boldsymbol{X}') = \int_0^\infty W(\boldsymbol{X} \to \boldsymbol{X}'; a)R^{st}(a|\boldsymbol{X})\,\mathrm{d}a, \qquad \text{etc} \tag{26}$$

are age-averaged transition probabilities.

The equivalence between (21) and (25) is a consequence of (15), (24) and (26): indeed, from these equations we have

$$\int_{\boldsymbol{X}'}\tilde{W}(\boldsymbol{X} \to \boldsymbol{X}')\,\mathrm{d}\boldsymbol{X}' = \int_0^\infty \mathrm{d}[-\psi(\boldsymbol{X}, a)]\left(\int_0^\infty \psi(\boldsymbol{X}, a)\,\mathrm{d}a\right)^{-1} = \left(\int_0^\infty \psi(\boldsymbol{X}, a)\,\mathrm{d}a\right)^{-1}. \tag{27}$$

Inserting (26) and (27) into (25), we recover (21).

Formally, (25) is similar with the stationary form of the phenomenological master equation (9). In spite of this formal coincidence, it is not possible, on the basis of (25), to calculate the bitemporal correlation functions $\langle X_i(t)X_j(t+\tau)\rangle$. This can be done only from the ADME. Obviously, only in the case of age-independent transition probabilities, (25) becomes a 'true' PME.

3. A scaling hypothesis

If the state variables $X_1, \ldots, X_s$ are extensive, a scaling hypothesis for ADME might be suggested by the classical one

$$W(\boldsymbol{X} \to \boldsymbol{X}') = Vw(\boldsymbol{X}/V; \Delta\boldsymbol{X}) = Vw(\boldsymbol{x}; \Delta\boldsymbol{X}) \sim V^1 \tag{28}$$

where V is the system extension,

$$x = X/V \qquad \text{and} \qquad \Delta X = X' - X \tag{29), (30}$$

(Van Kampen 1961, 1976, Kubo *et al* 1973, Kitahara 1975).

Taking into account (28), (19) leads to

$$R^{\mathrm{st}}(a|X)\,\mathrm{d}a = \omega(x)\exp(-aV\omega(x))\,\mathrm{d}(aV), \tag{31}$$

with

$$\omega(x) = V^{-1}\Omega(X) = \int_{\Delta X} w(X/V; \Delta X)\,\mathrm{d}\Delta X \sim V^0, \tag{32}$$

$$\Omega(X) = \int_{X'} W(X \to X')\,\mathrm{d}X' = V\int_{\Delta X} w(x; \Delta X)\,\mathrm{d}\Delta X \sim V^1. \tag{33}$$

Equation (31) suggest that the age a may be scaled as

$$a = \tau/V, \qquad \tau \sim V^0 \qquad \text{or} \qquad \tau = aV \tag{34}$$

and then

$$R^{\mathrm{st}}(\tau|x)\,\mathrm{d}\tau = \omega(x)\exp(-\tau\omega(x))\,\mathrm{d}\tau. \tag{35}$$

From (34), the following extension to age-dependent systems of (28) may be assumed:

$$W(X \to X'; a) = Vw(X/V; aV; \Delta X) \sim V^1, \qquad \Delta X = X' - X. \tag{36}$$

If (36) is valid, (19) and (26) become

$$\begin{aligned} R^{\mathrm{st}}(a|X)\,\mathrm{d}a = {}& \exp\left(-\int_0^{aV} \omega(X/V, \tau')\,\mathrm{d}\tau'\right) \\ & \times\left[\int_0^{\infty} \exp\left(-\int_0^{\tau''} \omega(X/V, \tau')\,\mathrm{d}\tau'\right)\mathrm{d}\tau''\right]^{-1} \mathrm{d}(aV), \end{aligned} \tag{37}$$

and

$$\begin{aligned} \tilde{W}(X \to X') = {}& V\int_0^{\infty} w(X/V; \tau''; \Delta X)\exp\left(-\int_0^{\tau''} \omega(X/V, \tau')\,\mathrm{d}\tau'\right)\mathrm{d}\tau'' \\ & \times\left[\int_0^{\infty} \exp\left(-\int_0^{\tau''} \omega(X/V, \tau')\,\mathrm{d}\tau'\right)\mathrm{d}\tau''\right]^{-1} \\ = {}& V\tilde{w}(X/V, \Delta X) \sim V^1, \end{aligned} \tag{38}$$

with

$$\omega(X/V, \tau') = \int_{\Delta X} w(X/V; \tau'; \Delta X)\,\mathrm{d}\Delta X \tag{39}$$

and thus the age-averaged transition probabilities are subjected to a scaling condition similar with (28). It follows that the 'phenomenological master equation' (25) can be solved by means of Van Kampen and Kubo-Matsuo-Kitahara approximations.

The physical meaning of (34)-(39) is clear: the age of a given state, $\boldsymbol{X}$, hyperbolically decreases with the increase of the system extension, V. One can see that an opposite behaviour is ascribed to the age in comparison with the relaxation time used in statistical mechanics (Landau and Lifschitz 1967), which increases with the extension of the system. This outlines the different nature of the two: whereas the age measures the persistence time of a state, the relaxation time measures the evolution time towards a given (equilibrium) state. Anyway, if the transition probabilities are age-independent, (34) is a consequence of the scaling condition (28), which is fulfilled by a broad class of physicochemical systems (Van Kampen 1961, 1976, Kubo *et al* 1973, Kitahara 1975).

4. Integration through Van Kampen and KMK approximations

Assuming the 'Van Kampen extensivity ansatz' (Van Kampen 1961, 1976):

$$\boldsymbol{X} = V\langle \boldsymbol{x}\rangle + V^{1/2}\boldsymbol{\mu} = V\boldsymbol{x} \qquad \langle \boldsymbol{\mu}\rangle = 0, \tag{40}$$

where

$$\langle \boldsymbol{x}\rangle = V^{-1}\langle \boldsymbol{X}\rangle = V^{-1}\int_{\boldsymbol{X}}\int_0^\infty \boldsymbol{X}\mathscr{P}^{\mathrm{st}}(\boldsymbol{X}, a)\,\mathrm{d}\boldsymbol{X}\,\mathrm{d}a, \tag{41}$$

expressing (25) in terms of the scaled probability

$$T^{\mathrm{st}}(\boldsymbol{\mu})\,\mathrm{d}\boldsymbol{\mu} = P^{\mathrm{st}}(\boldsymbol{X})\,\mathrm{d}\boldsymbol{X} = P^{\mathrm{st}}(V\langle \boldsymbol{x}\rangle + V^{1/2}\boldsymbol{\mu})\,V^{s/2}\,\mathrm{d}\boldsymbol{\mu}, \tag{42}$$

expanding the resulting equation and keeping the dominant terms in V, we have

$$\rho_j(\langle \boldsymbol{x}\rangle) = 0, \qquad j = 1, \ldots, s, \tag{43}$$

$$\tfrac{1}{2}\sum_i\sum_j B_{ij}(\langle \boldsymbol{x}\rangle)\partial^2_{\mu_i\mu_j}T^{\mathrm{st}}(\boldsymbol{\mu}) - \sum_i\sum_j A_{ij}(\langle \boldsymbol{x}\rangle)\partial_{\mu_i}(\mu_j T^{\mathrm{st}}(\boldsymbol{\mu})) = 0 \tag{44}$$

with

$$\rho_j(\langle \boldsymbol{x}\rangle) = \int_{\Delta \boldsymbol{X}} \Delta X_j \tilde{w}(\langle \boldsymbol{x}\rangle; \Delta \boldsymbol{X})\,\mathrm{d}\Delta \boldsymbol{X}, \tag{45}$$

$$A_{ij}(\langle \boldsymbol{x}\rangle) = \int_{\Delta \boldsymbol{X}} \Delta X_i \partial_{\langle x_j\rangle}\tilde{w}(\langle \boldsymbol{x}\rangle; \Delta \boldsymbol{X})\,\mathrm{d}\Delta \boldsymbol{X}, \tag{46}$$

$$B_{ij}(\langle \boldsymbol{x}\rangle) = \int_{\Delta \boldsymbol{X}} \Delta X_i \Delta X_j \tilde{w}(\langle \boldsymbol{x}\rangle; \Delta \boldsymbol{X})\,\mathrm{d}\Delta \boldsymbol{X}. \tag{47}$$

From (43) we can determine the steady values of the means $\langle x_1\rangle, \ldots, \langle x_s\rangle$. On the other hand, the normalised solution of (44) is given by

$$T^{\mathrm{st}}(\boldsymbol{\mu}) = (2\pi)^{-s/2}(\det \boldsymbol{C})^{-1/2}\exp(-\tfrac{1}{2}\boldsymbol{\mu}^{+}\boldsymbol{C}^{-1}\boldsymbol{\mu}), \tag{48}$$

(Van Kampen 1976), where the covariance matrix

$$\boldsymbol{C} = \langle \boldsymbol{\mu}\boldsymbol{\mu}^{+}\rangle$$

is the solution of the matricial equation

$$\boldsymbol{A}\boldsymbol{C} + \boldsymbol{C}\boldsymbol{A}^{+} + \boldsymbol{B} = 0, \qquad \boldsymbol{A} = \|A_{ij}\|, \qquad \boldsymbol{B} = \|B_{ij}\|. \tag{49}$$

The Van Kampen approximation fails when dealing with critical states. For such cases the more general method of Kubo, Matsuo and Kitahara (KMK) is recommended, which is based on the 'Kubo extensivity ansatz':

$$\Theta^{st}(\boldsymbol{x}) \sim \exp(VJ(\boldsymbol{x})), \qquad J(\boldsymbol{x}) \sim V^0, \tag{50}$$

(Kubo *et al* 1973), where

$$\Theta^{st}(\boldsymbol{x}) = V^s P^{st}(V\boldsymbol{x}). \tag{51}$$

Introducing the operator

$$\hat{\boldsymbol{p}} = V^{-1}\partial_x = \|\hat{p}_i\| = \|V^{-1}\partial_{x_i}\|, \qquad i = 1, \ldots, s \tag{52}$$

and the 'Hamiltonian'

$$\hat{H}(\boldsymbol{x}, \boldsymbol{p}) = \int_{\Delta X} \mathrm{d}\Delta \boldsymbol{X}\left[1 - \exp\left(-\sum_i \Delta X_i p_i\right)\right](\tilde{w}(\boldsymbol{x}; \Delta \boldsymbol{X}) \ldots) \tag{53}$$

equation (25) becomes

$$H(\boldsymbol{x}, V^{-1}\partial_x)\Theta^{st}(\boldsymbol{x}) = 0. \tag{54}$$

Substituting equation (51) into (54) and taking the dominant terms in V results in a stationary Hamilton-Jacobi equation:

$$H(\boldsymbol{x}, \partial_x J(\boldsymbol{x})) = 0, \tag{55}$$

and thus the integration of (25) reduces to the integration of the characteristic system attached to (55)

$$\mathrm{d}x_l/\partial_{p_l}H = \mathrm{d}p_l/-\partial_{x_l}H = \mathrm{d}J/\sum_i p_i\partial_{p_i}H, \qquad l = 1, \ldots, s, \tag{56}$$

where

$$p_i = \partial_{x_i}J(\boldsymbol{x}), \qquad i = 1, \ldots, s. \tag{57}$$

5. The principle of detailed balancing

For age-structured systems the detailed balance condition may be formulated as follows:

$$\int_0^\infty \mathcal{P}^{st}(\boldsymbol{X}', a')\, W(\boldsymbol{X}' \to \boldsymbol{X}; a')\, \mathrm{d}a' = \int_0^\infty \mathcal{P}^{st}(\boldsymbol{X}, a)\, W(\boldsymbol{X} \to \boldsymbol{X}'; a)\, \mathrm{d}a. \tag{58}$$

Equation (58) requires that the number of transitions from the state $\boldsymbol{X}'$ to the state $\boldsymbol{X}$ equals the number of reverse ones. Here we regard this principle merely as a hypothesis, the validity of which is to be checked in every particular situation.

Using equations (20) and (26), (58) may be given in an alternative form

$$P^{st}(\boldsymbol{X}')\, \tilde{W}(\boldsymbol{X}' \to \boldsymbol{X}) = P^{st}(\boldsymbol{X})\, \tilde{W}(\boldsymbol{X} \to \boldsymbol{X}'), \tag{59}$$

which, obviously, satisfies (25).

If (58) or (59) are fulfilled, then a straightforward solution for $P^{st}(\boldsymbol{X})$ and then for $\mathcal{P}^{st}(\boldsymbol{X}, a)$ is given by the Haken (1975) method, which is independent of the scaling hypotheses (34) or (36).

6. Equilibrium chemical fluctuations

The problem of chemical fluctuations has been extensively studied (Gardiner 1983). To illustrate the peculiarities of the above presented model, we shall consider a closed s component system, at equilibrium, involving a chemical reaction

$$\sum_{i=1}^{s} \nu_i^+ A_i \underset{k^-}{\overset{k^+}{\rightleftarrows}} \sum_{i=1}^{s} \nu_i^- A_i, \tag{60}$$

where $k^{\pm}$ are the forward and backward rate constants. The composition fluctuations of such systems may be described by means of a single extensive variable, the reaction extent, Ξ (De Donder 1936). This one may be expressed in terms of the numbers, N_i, of A_i molecules as follows:

$$\Xi = (N_i - N_i^*)/f_i, \qquad i = 1, \ldots, s \tag{61}$$

where

$$f_i = \nu_i^+ - \nu_i^- \tag{62}$$

and N_i^* are the most probable values of N_i $(i = 1, \ldots, s)$. Obviously, according to this definition, the most probable value of Ξ is 0.

Supposing that the stochastic version of the mass action law (Gardiner 1983) is valid, the equilibrium fluctuations may be expressed by means of a phenomenological master equation

$$\int W(\Xi' \to \Xi) P^{\mathrm{st}}(\Xi')\, \mathrm{d}\Xi' - \int W(\Xi \to \Xi') P^{\mathrm{st}}(\Xi)\, \mathrm{d}\Xi' = 0 \tag{63}$$

where

$$W(\Xi \to \Xi') = \sum_{\pm} \delta(\Xi - \Xi' \pm 1) V^{1-\Sigma_i \nu_i^{\pm}} k^{\pm} \prod_{i=1}^{s} [(N_i^* + f_i \Xi) \ldots (N_i^* + f_i \Xi - \nu_i^{\pm} + 1)], \tag{64}$$

and V is the system volume.

Within the framework of the KMK approximation the solution of (63) is the following

$$\begin{aligned}\Theta^{\mathrm{st}}(\xi)\, \mathrm{d}\xi &= P^{\mathrm{st}}(\Xi = V\xi) V\, \mathrm{d}\xi \\ &= \exp\{-V \textstyle\sum n_i^* \ln(1 + f_i\xi/n_i^*) - V\xi \sum f_i[\ln(1 + f_i\xi/n_i^*) - 1]\} \\ &\quad \times \left(\int \exp\{-V \textstyle\sum n_i^* \ln(1 + f_i\xi/n_i^*) - V\xi \sum f_i[\ln(1 + f_i\xi/n_i^*) - 1]\}\, \mathrm{d}\xi \right)^{-1}\end{aligned} \tag{65}$$

where

$$\xi = \Xi/V \qquad n_i^* = N_i^*/V, \tag{66}$$

and

$$k^+/k^- = \prod_{i=1}^{s} (n_i^*)^{f_i} \tag{67}$$

(Vlad *et al* 1984b).

Our present method allows in addition to evaluate the statistical properties of the age of a fluctuation state. The direct application of (31), (35) and (63) leads to

$$R^{\mathrm{st}}(a|\Xi = V\xi)\, \mathrm{d}a = \omega(\xi) \exp(-aV\omega(\xi))\, \mathrm{d}(aV), \tag{68}$$

with

$$\omega(\xi)=\sum_{\pm} k^{\pm} \prod_{i=1}^{s} (n_i^* + f_i\xi)^{\nu_i^{\mp}}, \tag{69}$$

which evidently fulfils the scaling condition (34). The moments corresponding to (68) are

$$\langle a\rangle_\xi = \omega^{-1}(\xi)\, V^{-1} \tag{70}$$

$$\langle \Delta a^2\rangle_\xi = \omega^{-2}(\xi)\, V^{-1}, \ldots . \tag{71}$$

Equations (68), (70) and (71) are generalisations of the relationships derived by Šolc (1974) in the case of chemical equilibrium $A_1 \rightleftarrows A_2$, by applying a different approach.

The next step could be to generalise the classical stochastic model of mass action law, considering that the reaction rates are age-dependent. Moreover, we may assume that they obey the scaling condition (36), i.e.

$$k^{\pm} = k^{\pm}(aV). \tag{72}$$

The age dependence would be plausible in the case of fast processes, for which the regression of fluctuations towards equilibrium is non-Markovian. Evidently, this approach is purely phenomenological.

Taking into account (72), after simple but lengthy manipulations the KMK approximation leads to

$$\Theta^{\mathrm{st}}(\xi) \sim \exp\left[V\left(\int \ln \Gamma(\boldsymbol{n}^*, \xi)\, \mathrm{d}\xi - \sum_i (n_i^* + f_i\xi) \ln(1 + f_i\xi/n_i^*) + \xi \sum_i f_i \right)\right] \tag{73}$$

where

$$\boldsymbol{n}^* = \|n_i^*\|, \qquad f = \|f_i\|, \qquad i = 1, \ldots, s, \tag{74}$$

$$\Gamma(\boldsymbol{n}^*, \xi) = \left(\int_0^\infty k^+(\tau)\beta(\boldsymbol{n}^* + \boldsymbol{f}\xi, \tau)\, \mathrm{d}\tau \right)\left(\int_0^\infty k^-(\tau)\beta(\boldsymbol{n}^*, \tau)\, \mathrm{d}\tau \right)$$
$$\times \left(\int_0^\infty k^-(\tau)\beta(\boldsymbol{n}^* + \boldsymbol{f}\xi, \tau)\, \mathrm{d}\tau \right)^{-1} \left(\int_0^\infty k^+(\tau)\beta(\boldsymbol{n}^*, \tau)\, \mathrm{d}\tau \right)^{-1}, \tag{75}$$

$$\beta(\boldsymbol{n}^*, \tau) = \exp\left(-\sum_{\pm} \prod_i (n_i^*)^{\nu_i^{\mp}} \int_0^\tau k^{\pm}(\tau')\, \mathrm{d}\tau' \right), \qquad \text{etc}, \tag{76}$$

and $n_1^*, \ldots, n_s^*$ fulfil the condition

$$\tilde{K}(\boldsymbol{n}^*) = \prod_{i=1}^{s} (n_i^*)^{f_i}, \tag{77}$$

with

$$\tilde{K}(\boldsymbol{n}^*) = \int_0^\infty k_j^+(\tau)\beta(\boldsymbol{n}^*, \tau)\, \mathrm{d}\tau \left(\int_0^\infty k_j^-(\tau)\beta(\boldsymbol{n}^*, \tau)\, \mathrm{d}\tau \right). \tag{78}$$

Equation (77) is similar to the thermodynamic equilibrium condition for ideal systems (67) with the difference that, due to the age dependence, $\tilde{K}$ is no longer constant. Its dependence on $\boldsymbol{n}^*$ is given by (78).

7. Conclusions

Our approach leads to a better understanding of the behaviour of physical systems described by a PME which obeys (25). The main result is given by (31): the age distribution of a fluctuation state is exponential and is subjected to the scaling condition (34). This property is applicable to a large class of natural phenomena, such as generation-recombination events in semiconductors, chemical fluctuations, etc.

The introduction of age-dependent transition probabilities leads to a new type of stochastic process, somewhat similar to the theory of continuous time random walks (CTRW) (Montroll and West 1979). As well as the CTRW, our approach is purely phenomenological.

Even if the transition probabilities are age-dependent, the stationary states may be described formally by means of a 'phenomenological master equation'. Unfortunately, this method is of restricted applicability. Thus, even at equilibrium, the evaluation of the temporal correlation functions cannot be reduced to the integration of a phenomenological master equation. The approach is limited to the evaluation of fluctuations at a given instant.

To simplify the integration methods we introduced an age scaling condition ($a = \tau/V \sim V^{-1}$), affording the application of Van Kampen and Kubo-Matsuo-Kitahara approximations.

The scaling condition for the age arose from purely heuristic considerations: its validity was rigorously proved for Markovian systems obeying (28), and then extended to age-dependent case. This procedure is open to discussion.

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